LABORATORY EXERCISE NO. 3
POTENTIOMETRIC TITRATION

Objective: Determination of an acid concentration in solution by potentiometric titration method.

Theoretical background

Quantitative studies of reactions in solutions are often carried out using a technique known as *titration*. In titration, a solution of accurately known concentration, called a *standard solution* or *titrant*, is added gradually to another solution of unknown concentration, until the chemical reaction between the two solutions is complete. This state is known as the *end point of a titration* or *equivalence point*. If we know the volumes of the standard and unknown solutions used in the titration, along with the concentration of the standard solution, we can calculate the concentration of the unknown solution. The end point of a titration may be determined by several methods, e.g. conductometric, potentiometric, photometric, visual indicator, etc.

Potentiometric titration is based on determination of an equivalence point by results of potentiometric measurements. Near the equivalence point there is a sharp change (jump) of potential of an indicator electrode. It is observed, if the electrode is reversible even to one of substances participating in chemical reaction that is proceeding at titrant addition. So, for the acid-base titration the electrodes reversible to hydrogen ions are used, at determination of the chloride ions – silver-silver chloride, etc. During the titration nondissociated substances (water, complexes or deposits) are formed in analyzed solution. Similar to others titration methods, the reactions proceeding at potentiometric titration should proceed with the high speed, be irreversible and strict in stoichiometric relationship. Potentiometric titration is used basically for determination of electrolyte concentration, but it is possible to use it for determination of dissociation and complexation constants. Besides potentiometric titration allows to determine concentration of acids or bases differing in strength at their simultaneous presence in solution. It would be necessary that their dissociation constants differ more than 10000 times, only at this condition the neutralization of one of electrolyte in their mixture came after the end of titration of another.

For realization of potentiometric titration, as a rule, cell with the transfer, consisting of the indicator electrode shipped in analyzed solution and the reference (comparison) electrode are used. As reference electrode calomel or silver-silver chloride electrodes are often used. For example, the cell

Indicator electrode | investigated solution || KCl (solution) |AgCl |Ag.

The EMF of this cell is determined by the expression

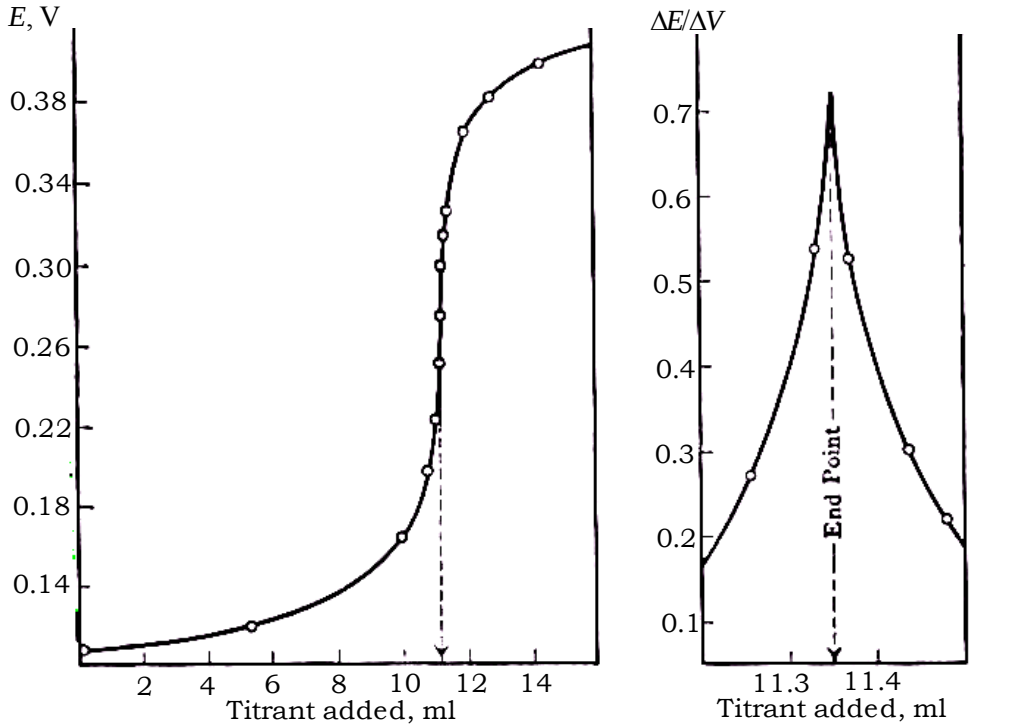
$$E = \varphi_{ref} - \varphi_{ind}, \quad (1)$$

where φ_{ref}, φ_{ind} – potentials of reference and indicator electrodes. During the titration φ_{ref} value remains constant, so the measured EMF changes at addition of the titrant is determined by changes in φ_{ind} only.

During the pothentiometric titration the small portions of titrant are gradually added to investigated solution and after each addition the measurement of the EMF value is carried out. Suppose, for example, a standard solution of silver nitrate is being titrated by means of a solution of sodium chloride. As the titration proceeds, silver chloride is precipitated, and the concentration of the silver ions remaining in solution decreases steadily. The potential of a silver electrode, which in this case acts as the indicator electrode changes correspondingly. The change of potential is quite small, at first, since a hundredfold decrease of concentration alters the potential by only 0.118 volt. However, when the end point of the titration is approached the *relative* change of concentration of silver ions for a given amount of sodium chloride added increases rapidly. There is a corresponding rapid change in the silver electrode potential, for the reason stated above. The end point can thus be found by determining the quantity of titrant added when the rate of change of the electrode potential is a maximum. A silver electrode can thus be used as an indicator for the quantitative analysis of chloride solutions, or of solutions of any anion forming an insoluble silver salt, e.g. bromide, iodide, cyanide, thiocyanate and phosphate. Other metal electrodes may be adapted to the analysis of other anion solutions.

An equivalence point may be determined using jump (sharp decrease or increase) of EMF that is observed due to high relative change of concentration of a determined ion at transition through an equivalence point. Exact value of an equivalence point is found on a curve of titration (Fig. 1). On the graph in coordinates «EMF – titrant volume added» a vertical, or, at

least, the closest to vertical, part of the S-shaped curve, corresponds to a equivalence point. This graph is known as *integral curve*. In order to determine the position of the end point with some degree of precision, it is necessary to find the point at which the slope of the titration curve is a maximum. The method adopted to find this point, is to draw the ratio of the change of the EMF (ΔE), that corresponds to the addition of a definite small volume (ΔV) of titrant solution, to the ΔV value, that is, $\Delta E / \Delta V$, against the total volume of titrant added. Provided ΔV is not large, so the ratio $\Delta E / \Delta V$ is a close approximation to the slope of the integral titration curve in Fig. 1 (a), and it has a maximum value at the end point, as shown in Fig. 1 (b). The height of this maximum, and the accuracy with which the end point can be estimated, are smaller the more dilute the solutions being titrated and the more soluble the precipitated salt. Also the equivalence point can be determined by using a *differential curve of the second order* – dependence of $\Delta^2 E / \Delta V^2$ value on titrant added volume. Here equivalence point corresponds to the zero value of this function because function derivative in a extreme point is equal to zero. Determination of a equivalence point by using differential curves is much more precise, than from simple dependence of E on V.



a) Integral Curve b) Differential Curve

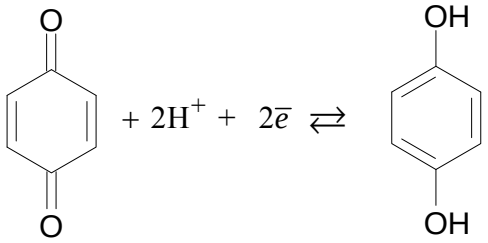
Fig. 1. Potentiometric titration curves

The principles described above can be used for other forms of titration. For example, in the titration of an acid solution by a base, there is a rapid relative change in the hydrogen ion concentration as the end point is reached. The position of this point can consequently be obtained from measurements of the potential of a suitable hydrogen indicator electrode, in the same way as a silver electrode in the precipitation titration. The accuracy of the neutralization titration depends on the concentration of the solutions, and also on the strength of the acid and base; if the acid or base, or both, are too weak, the point at which $\Delta E / \Delta V$ is a maximum cannot be detected satisfactorily and accurate titration is not possible. Titrations involving conventional oxidizing and reducing agents, e.g., permanganate or dichromate ions, can also be followed potentiometrically; here again the potential of the system undergoes a rapid change at the end point, provided the oxidation and reduction reactions go to virtual competition. The indicator electrode employed for this type of titration consists of an inert metal, such as platinum.

The potentiometric titration procedure can be employed with colored solutions, and often in dilutions at which ordinary titrations with colored indicators would be very inaccurate. The general method is to place the indicator electrode in the solution to be titrated and to combine it with a reference electrode of constant potential, e.g., calomel or silver chloride electrode, thus forming a complete cell. The EMF of this cell is measured, by a suitable potentiometer, as various known amounts of titrant solution are added. The actual potential of the indicator electrode need not be known; since the potential of the reference electrode remains constant, the EMF of the complete cell will undergo the same changes as does the potential of the indicator electrode. The end point of the titration is then the point at which $\Delta E / \Delta V$ is a maximum, where ΔE is given by the changes in the EMF of the cell. Numerous devices have been developed in order to simplify the titration procedure, and to increase the ease and accuracy of determining the end point.

The acid-base potentiometric titration

Glass electrode or quinhydrone electrode are used usually for the realization of the acid-base potentiometric titration. Quinhydrone electrode is an oxidation-reduction electrode and represents the platinum plate or wire immersed in solution, that contains quinone ($C_6H_4O_2$), hydroquinone ($C_6H_4(OH)_2$) and hydrogen ions. At work of this electrode the following reaction proceeds



The potential of this electrode according to Nernst equation is determined by expression

$$\varphi = \varphi^o + \frac{RT}{F} \ln c_{H^+}, \qquad (2)$$

where φ^o – standard electrode potential; c_{H^+} – concentration of hydrogen ions in solution.

Quinhydrone electrode is reversible to hydrogen ions in acid and alkaline solutions. In a strong alkaline media the potential of the electrode practically does not depend from the pH value because hydroquinone is completely dissociated.

For using of quinhydrone electrode as an indicator electrode a small amount of quinhydrone (equimolar mixture of quinone and hydroquinone) is added to a solution and a platinum plate or wire sealed in a glass tube must be immersed to the solution.

Potentiometric acid-base titration allows to carry out determination of concentration of components in a mixture of acids if they differ in strength not less than on four order. For example, at titration of the mixture containing hydrochloric and acetic acids, there are two jumps on a potentiometric titration curve. The first of them corresponds to the end of HCl titration, the second jump is observed at full neutralization of an acetic acid. Also several jumps have titration curve of the multibase acids, which stepwise dissociation constants essentially differ, for example, for chromic or phosphoric acids.

Experiment and calculations

1. For the determination of acid concentration by potentiometric titration method the galvanic cell with transfer consisting from quinhydrone and saturated silver-silver chloride electrodes is used

Ag | AgCl, KCl (solution) || investigated solution, $C_6H_4O_2$, $C_6H_4(OH)_2$ | Pt

According to the Nernst equation the EMF of this cell, at constant concentration of the KCl in solution, is given by

$$E = E^o + \frac{RT}{F}\ln c_{H^+} = E^o - \frac{2.303RT}{F}\text{pH}, \qquad (3)$$

where E^o – standard electromotive force (EMF) of the cell.

2. In a vessel for titration pour defined volume of analyzed solution of an acid or a mix of acids and dilute with distilled water up to such volume that electrodes were completely immersed in a solution, switch on magnetic mixer, then add a small amount of quinhydrone. Measure the EMF value of the galvanic cell by pH meter-millivoltmeter.

3. In the beginning make *rough titration* for the determination of volume of alkali solution necessary for the reaching of jump(s) of the EMF. In the rough titration add the alkali solution in the equal portions of 1 mL and each time measure and write down the EMF value of the cell. After finishing of rough titration and determination of titrant volume(s) where there is the greatest change of the EMF.

4. Carry out the *accurate titration*. Its difference from rough titration is that in the region of EMF jump alkali solution is added by the portions of 0.1 mL. The important condition of exact determination of equivalence point is addition of alkali solution after EMF jump for providing 5-6 measurements for a possibility of drawing the differential titration curve. Results of measurements write down to the following table:

c_{NaOH} = ... mol/L		V_{HA} = ... mL
V_{NaOH}, mL	E, mV	$\Delta E / \Delta V$

5. Draw titration curves using the EMF data obtained in exact titration. Integral titration curve is a plot in coordinates «EMF – volume of titrant added» and differential curve of the first order is a plot in coordinates «$\Delta E / \Delta V$ – volume of titrant added».

6. Determine equivalence point(s) using curves drawn according to Fig. 1.

7. Calculate the concentration of the acid in the investigated solution by the formula

$$c_{\mathrm{HA}} = c_{\mathrm{NaOH}} \frac{V_{e.p.}}{V_{\mathrm{HA}}}, \qquad (4)$$

where $V_{e.p.}$ – volume of alkali solution added in equivalence point; V_{HA} – volume of acid solution taken for titration; c_{NaOH} – concentration of the alkali used.

If for the titration the mixture of acids was taken, the concentration of a strong acid is calculated using mentioned above equation. Taking into account that all alkali added till to the first equivalence point, goes for neutralization of a strong acid, for calculation of concentration of a weak acid the following equation must be used

$$c_{\mathrm{HA}} = c_{\mathrm{NaOH}} \frac{V_{e.p.2} - V_{e.p.1}}{V_{\mathrm{HA}}}, \qquad (5)$$

where $V_{e.p.1}$ – volume of alkali in the equivalence point of a strong acid, $V_{e.p.2}$ – volume of alkali in equivalence point of a weak acid.