POTENTIOMETRY

Potentiometry is one of the methods of electroanalytical chemistry. In potentiometric measurements, the potential between two electrodes is measured using a high impedance voltmeter. It is usually employed to directly find the concentration of a solute in solution or as a potentiometric indication of equivalence in titrations.

An electrode is represented by for example two-phase system metal/solution of metal ions, where the ions or electrons can transit from one phase to another. In case of equilibrium an electric bilayer is produced on phase dividing line. This bilayer is the principle of potential difference, labelled as equilibrium electrode potential.

For metal electrode with reversible potential, submerged into solution, that contains metal ions we can define Nernst equation:

$$E_M = E^0_M + 0.0591/z * \ln a_M z^+$$

Where, E_M – potential of metal electrode; E^0_M – standard potential of electrode (potential when activity of M^{z+} ions in solution equals to 1); $a_M z^+$ - activity of M^{z+} ions in solution.

It is apparent from the equation that potential of metal electrode is logarithmical function of activity of ions in the solution. The ten times difference of activity of ion with charge number = 1 will result in 59.2 mV change of electrode potential. In diluted solution the measured activity of ions can be integrated with ion concentration.

Electrochemical cell, electrodes, apparatus. The absolute values of electrode potential can not be measured. We can measure the relative value from difference of potentials of two electrodes as voltage of electrochemical cell consisted of reference electrode with constant potential and second electrode for which we measure the potential. This electrode is called indicator electrode and is chosen based on the evaluated system so its potential is function of activity of measured ion in the solution.

The refence base is standard hydrogen electrode, for which the standard potential at all temperatures was defined as zero.

In practice the following electrodes of type II are used as the refence electrodes:

Calomel electrode – the most common reference electrode. It consists of mercury covered by layer of calomel, in KCl solution. The potential of electrode is dependent only on concertation of Cl^- ions in electrolyte with which the electrode is filled. Based on the used concentration of KCl we distinguish several types of calomel electrodes. The most common one is the saturated calomel electrode, in which the concentration of saturated KCl solution is easily maintained by addition of few KCl crystals.

Chloride-silver electrode – consist of Ag wire, on which a thin layer of AgCl is applied electrolytically. Its potential is dependent on concentration of Cl^- ions in solution.

The following metal electrodes (type I) are most commonly used as indicator electrodes:

Silver electrode – its potential is function of activity of Ag^+ ions.

Platinum electrode – it consists from shiny platinum sheet or wire. In particular, it is used as electrode from inert metal for measurement of reduction potential $E_{ox/red}$ of redox systems.

Antimony electrode – one of the oxide electrodes. Its potential is function of activity of H_30^+ ions in solution.

Besides the type I and type II electrodes, where the principle is based on electrochemical (or redox) potential, we can use also electrodes of membrane type. Their equilibrium potential is defined by membrane potential, which is created on dividing line between two electrolyte solutions divided by a membrane which is not in the same way permeable for different ions (electrochemical membrane). The principle of membrane potential is ion-exchange equilibrium on phase dividing line.

In membrane electrodes the measured and reference solutions are divided by membrane from suitable material. The membrane electrode consists of internal reference electrode, internal solution and membrane, which is submerged into measured solution with external reference electrode. Potentials of both reference electrodes are constant.

Membrane electrodes include glass electrode and ion-selective electrodes (ISE).

Glass electrode – is the most important and most selective electrode for H_30^+ ions. The requirement for proper function is creation of hydrated layer of orthosilicic acid gel, where the ion-exchange reaction between Na^+, K^+ in glass and H_30^+ ions in solution. Because of this the glass electrode needs to be soaked in water for several days before the measurement and after the measurement it need to be stored in water or buffer solution based on the requirements of manufacturer. Calibration of the method on buffer solutions need to be checked occasionally.

Apparatus – terminal voltage of electrochemical cell, which is measured, represents the difference between positive and negative electrode. Therefore, the measurement of voltage need to be performed in conditions where almost no current which can cause polarisation of electrode is going through system. This requirement is fulfilled in case of different types of electronic millivoltmeters. They have big input resistance; therefore, they can be used for measurement of cells with high internal resistance for example cells with glass electrode, ion-selective electrode or measurements in non-aqueous conditions. These apparatuses are called pH meters and measure in pH or mV units. The modern ones are produced as digital and have high precision of measured values. The digital signal can be then used for further processing.

Because the measured values of pH are affected by temperature, the pH meters contain potentiometer for setting the temperature of measured solutions or automatic temperature compensation using resistance thermometer.

TITRATION WITH POTETIOMETRIC INDICATION

The equilibrium point during the potentiometric titrations is identified based on potential of suitable indicator electrode. The potential of this electrode is dependent on activity of measured ion or ion in measured solution.

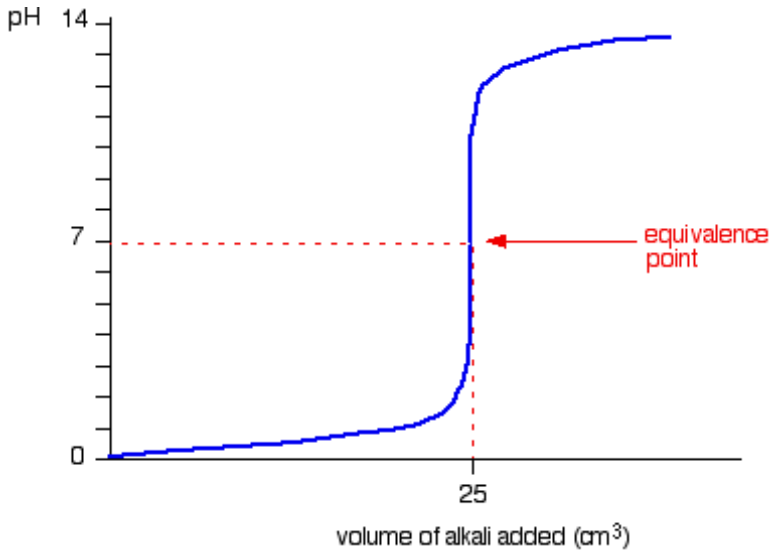
Advantages of potentiometric titration:

- Better precision of equilibrium point indication
- Higher sensitivity – can be used in more diluted solutions
- Applicable also in cases, where the visual indication is not possible

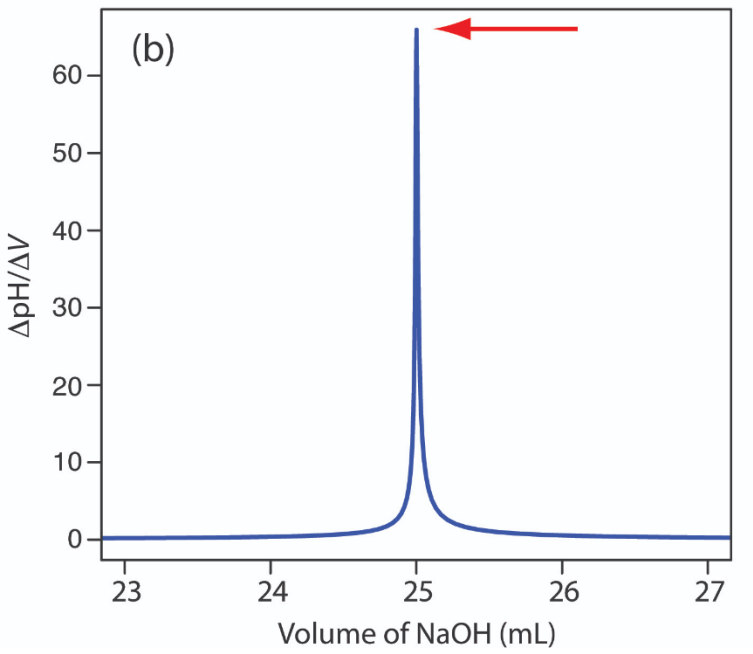
Almost all indicator electrodes are suitable for potentiometric titration. The glass electrode is suitable especially for acid-base titration. Platinum electrode is suitable for redox titrations.

Silver electrode for precipitation electrodes and ion-selective electrodes for titration where a complex is created.

The change of potential of indicator electrode based on volume unit of volumetric solution (titrant) added to the measured solution during the titration will get bigger until it reaches the maximal value in the equilibrium point. Graphical illustration of dependence of measured values of voltage to volume of added volumetric solution is called titration curve (see figure below). The inflex point in symmetrical curves is identical with equilibrium (equivalence) point.



If we look at change of measured current from previous measurement (ΔpH) divided by change of added volume from previous measurement (ΔV) and we will do the graph of these values – dependence of ratio ΔpH/ΔV to volume of added volumetric solution we will get the following figure – the maximal point in this figure equals to the equilibrium point of the titration.



Procedures for potentiometric titrations

Potentiometric titrations are done in beaker of sufficient volume (the beaker should be filled up to ½ of the volume). We add a magnetic stirrer to the bottom of the beaker and add the prescribed amount of sample solution. The electrodes are rinsed with water and placed inside the sample solution so the ends of electrodes are submerged but are not touching the bottom of the beaker so they cannot be damaged by the stirrer.

A burette with volumetric solution (titrant) is prepared and placed so we have good access to the shutter of the burette. It is advised to extend the end of the burette with narrow capillary, so it is submerged in the titrated solution and allows the addition of the prescribed volumes of volumetric solution.

After connecting the electrodes, we will turn on the stirring, set up the apparatus a we will do the first titration by adding the volumetric solution in 1-2 mL equivalents. After each addition we will wait several seconds until the solution is thoroughly mixed and the value of the current (E) is constant. We will fill up a table with volumes of volumetric solution added (mL) and with measured values E [mV] for each addition. We will also calculate the value of ΔE/ΔmL which is the difference of two neighboring measured values of E in mV divided by difference of corresponding volumes that were added. Before the equilibrium point, which is indicated by increasing values of ΔE/ΔmL, we will start adding the volumetric solution by smaller volumes (ideally constant – for example 0.1 mL). The titration can be ended after we measure several values after the equilibrium point (when the ΔE/ΔmL values will start to drop).

When we titrate the solution of completely unknown concentration, we can do an informative first titration – i.e. we will add the volumetric solution in bigger volumes and we will identify the approximate interval (in mL) where the equilibrium point will be. Then we will do the titration once again but around the approximate equilibrium point we will add the volumetric solution in smaller volumes (0.1 or 0.2 mL) – so we can identify the equilibrium precisely. After the titration we need to rinse the electrodes with water. The determination is done at least twice and we will calculate the mean value from both determinations.

Interpretation of results

From the table of measured values of E and the corresponding volumes of volumetric solution we can determine the equilibrium point by calculation of from graphical illustration.

V [mL]	E [mV]	ΔE/ΔV	Δ^2 E
6	160	= (186-160) / (8-6) = 26 / 2 = *13*	
8	186		
8.5	198	= (198-186) / (8.5-8) = 12 / 0.5 = *24*	= 24 – 13 = 11
8.6	205	*70*	46
8.7	216	*110*	40
8.8	230	*140*	30
8.9	258	*280*	60
9.0	294	*360*	80
9.1	317	*230*	-130
9.2	327	*100*	-130

The equilibrium point can be calculated using the interpolation equation:

$$V_{ekv} = V_1 + k^* (a / a\text{-}b)$$

Where, V_1 – the volume of volumetric solution added before the biggest value of $\Delta E/\Delta V$ – in our case it is 8.9 mL

k – is $V_1 – V_2$ – difference of individual volumes added to the solution – in our example = 9.0 – 8.9 = **0.1 mL**

a – the last positive value of Δ^2 E corresponding to volume V_1 – in our example = 80

b – the first negative value of Δ^2 E corresponding to volume V_2 – in our example = -130

then:

$$V_{ekv} = V_1 + k^* (a / a\text{-}b) = 8.9 + 0.1^* (80/80\text{-}(-130)) = 8.9 + 0.1^* (80/210) = 8.9 + 0.04 =$$

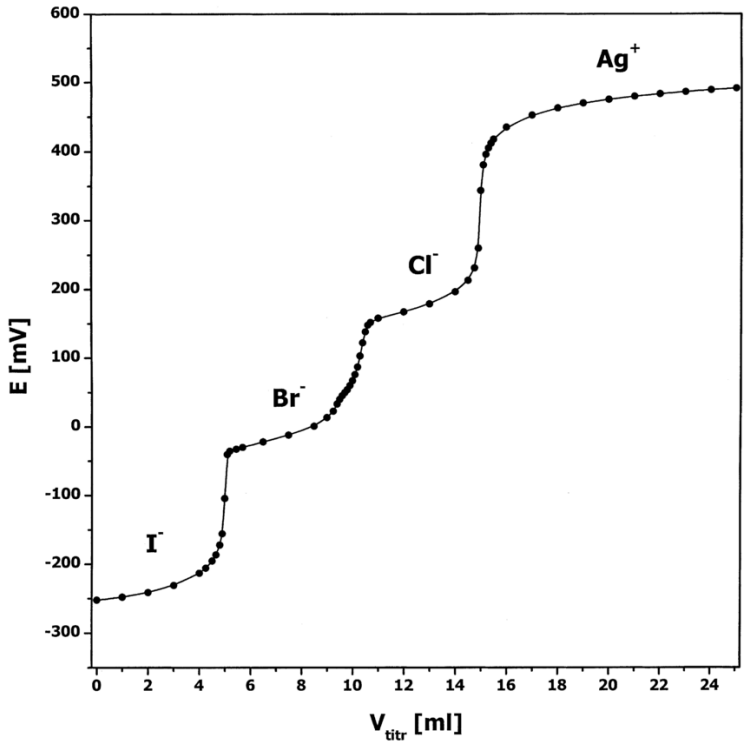
8.94 mL

In our example the equilibrium point is at volume of 8.94 mL of volumetric solution added.

Besides the above-mentioned interpretations of potentiometric titrations by employing simple apparatuses, the automatic titration apparatuses, where the equilibrium point is indicated directly by measuring device or the titration is carried out by computer are used more frequently in the last years.

Task for the practice – Simultaneous determination of halogenates

The simultaneous determination of halogenates – I^-, Br^- and Cl^- - is possible based on different solubility of silver salts. During the titration with $AgNO_3$ solution the least soluble AgI ($K_s = 10^{-16}$) is produced first, then AgBr ($K_s = 10^{-13}$) and finally AgCl ($K_s = 10^{-10}$). So in this case three equilibrium points can be observed on the titration curve.



The volume until the first potential 'jump' equals to amount of I^-, the difference between the first and second jump is equal to amount of Br^-, and the difference between the second and third jump equals to Cl^-. The difference in solubility allows (in some conditions) the simultaneous determination of all three ions. The simultaneous determination of I^- and Cl^- is without problems.

For this determination, the silver electrode is used as indicator electrode and calomel electrode is used as reference electrode, which is added to the measured solution through slat bridge filled with 10% solution of KNO_3 – so the KCl from calomel electrode is not introduced to the titrated solution.

Chemicals and solutions

Solution of silver nitrate – c($AgNO_3$) – ca. 0.03 mol/l, 10% solution of KNO_3, solution of KCl for standardization of $AgNO_3$ solution.

Procedure for determination of sample

We will pipette 10 mL of the sample containing I^- and Cl^- to 150 mL beaker a we will dilute with distilled water to approximately 70 mL. We will titrate with solution of $AgNO_3$ according to common procedures of potentiometric titration. Around the equilibrium points we will titrate with 0.1 mL equivalents.

Procedure for standardization of $AgNO_3$ volumetric solution

We will pipette 20 ml of KCl solution (c = 0.01336 mol/L) to 150 mL beaker, dilute it with distilled water to approximately 70 mL and titrate with $AgNO_3$ solution.

Interpretation of results

In report provide the table of measured values – added volume in mL, measured current in mV, $\Delta E/\Delta V$ and Δ^2 E. Provide the graphical illustration of dependence of mV on volume of volumetric solution. Determine the equilibrium points using the interpolation equation. Calculate the weight (in mg) of I^- and Cl^- in 100 mL of sample.