Task No. II

DETERMINATION OF Al_2O_3 POINT OF ZERO CHARGE

I. Goal of the Task

The goal of the task is determination of the point of zero charge (PZC) of alumina oxide that is the value of pH when charge density is equal to zero. PZC is determined by the Ahmed's method.

II. Theoretical problems

1. Mechanism of charge formation of interface.
2. Electric double-layer.
3. Point of zero charge (PZC).
4. Isoelectric point (IEP).

References:

1. G. Kortüm, *Elektrochemia*, PWN Warszawa, 1966, str. 346–350, 462–464.
2. W. Janusz, *Koloidy"*, Wydział Chemii UMCS, Lublin, Ćwiczenie nr 4, „Wyznaczanie ładunku i punktu zerowego PZC trudnorozpuszczalnych tlenków metodą miareczkowania potencjometrycznego".
3. H. Sonntag, *Koloidy*, PWN Warszawa, 1982, str. 74–88.
4. Praca zbiorowa, *Chemia fizyczna*, PWN Warszawa, 1966, str. 764–766.
5. E. T. Dutkiewicz, *Fizykochemia powierzchni*, WNT Warszawa, 1998, str. 45–51.

III. Theoretical part

III. 1. Chemical potential

On the homogeneous surface of solid or liquid phase (even pure metal in vacuum) usually change in electric charge distribution (density) proceed. This is the case of formation of the areas with changeable potential whose thickness is a few particles size. In the case of two contacting layers (especially solid-solution or metal-solution) there exists the tendency for attraction of charged molecules (electrons, ions) in different ways by two layers. Dipole particles will preferentially adsorb at the interface. The formed electric field can cause polarization effects in the neighbouring molecules. All these effects lead to formation of potential differences between the inside of both phases. It is the **Galvani potential** φ. Generally, the Galvani potential difference is measurable only when the two phases have an identical chemical composition. This potential is equal to the total work done in charge transfer from one phase to another. This value is difficult to determine because it depends on the character of unit load charge. The smallest charge is electron, which shows some chemical properties and can react with a phase component. Change of system energy caused by passing actual electric charge from one phase to another can not be a measure of electrochemical potential changes. Theoretical charge in the electrostatic theory is infinitesimal, and its introducing to the environment does not cause changes in charge distribution and dipole orientation.

The electrostatic potential near the phase is easy to measure because it is the work done in transfer of point of electric charge from infinity to the point near the surface limiting the phase. This point is located outside the phase in a distance where the potential obtains the largest value. Its value decreases with the distance in accordance with the Coulomb law. The difference of exterior potentials is called the contact potential or the Volta potential difference ψ.

It is worth mentioning about the **surface potential** χ result from polarization effects and the dipole layers existing on the surface which can form for different reasons. For instance in metals displacement of positive and negative (electrons) charges takes place but in solutions stable dipoles accumulate on the boundary surface. As a result. the electrical double-layer is formed. The potential jump formed by the dipole layer on the surface is called the surface potential χ. The sum of Volta and surface potentials is the electric interior phase potential φ and it is called the inner potential or the **Galvani potential (macro potential)**

$$\varphi = \psi + \chi \qquad (1)$$

The first term is usually considered as connected with the total transition of charges from one phase to another, whereas the second term is connected with other microscopic changes at the interface.

Zeta potential ζ is the electric potential in the interfacial double layer at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.

III. 2. Mechanism of charge formation at the interface

The presence of electric charge in the system is connected with potential differences. The most important mechanisms of charge formation at the interface are:

1. Difference in electron affinity (two metals or metal/conductor) In the solid-liquid, liquid-liquid systems this mechanism is meaningless except for dispersed mercury and metal salts.
2. Difference in ions affinity of positive or negative charge for these two phases:
   - ions division between two phases (oil and water),
   - ions adsorption from an electrolyte on the solid surface,
   - predominance of one ion type dissolving on the other one in crystal lattice. Every time the equilibrium is formed when electrochemical potentials in the case of ions, which can spontaneously pass by interface, equalize in both phases; e.g. AgI- electrolyte Ag^+ or I^- can change the proportion Ag^+/I^- on the deposit surface. With the determined concentration the ions Ag^+ and I^-number will be the same, there is no charge excess- **point of zero charge**
3. Surface groups ionization.

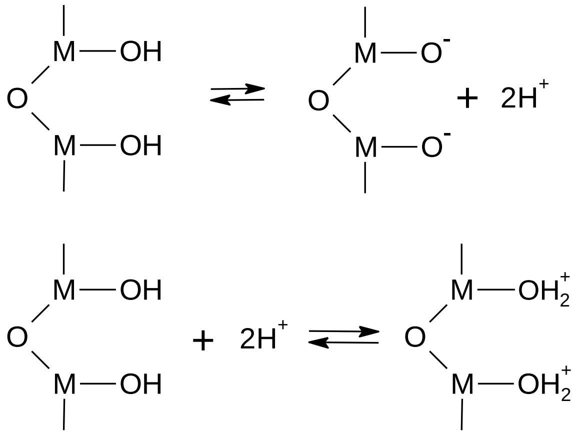
   Surface groups ionization takes place in chemical compounds possessing on the surface some groups e.g. carboxyl, amine or on the surface of insoluble metal oxides. In these systems size and sign of the potential depend on solution pH. Potential formation ions, on the solid surface are H^+ and $OH^–$. It is because $OH^–$ ions can be considered as equivalent to the component ions in the crystal lattice (oxygen), while H^+ can replace metal ions, although actually they are amphoteric dissociation reactions. Metal oxide crystals have ionic structure, on isolated from the environment their surface uncompressed local electric charges occur from originating incompletely coordinated ions M^{n+} and $O^{2–}$. As a result oxides are capable of to surface reactions. In the reaction with water the M–OH groups are created, their hydrogen ions are active and can diffuse inside the solution. This causes formation of negative charge which counteracts ions diffusion into the solution. In this way, the equilibrium is established. This state corresponds with the defined values of charge and surface potential and pH of solution. H^+ ions adsorption from solution can occur too, because of that only $OH^–$ ions remain in the solution.

Therefore:

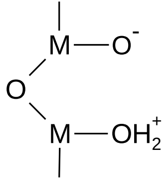
$$–MOH \longleftrightarrow –MO^– + H^+ \qquad (2)$$

$$–MOH + H_2O \longleftrightarrow –MOH_2^+ + OH^– \qquad (3)$$

The surface groups –M–OH have amphoteric character and dissociate. The process of charge formation on the surface can be schematically shown:



As a result of this reaction positive or negative charges accumulate on the oxide surface. Oxygen ions role as potential creating ions is explained too for the metal oxide/electrolyte solution systems. When in solution only H^+ and OH^- are present and the surface possesses zero charge then:



but the number of positively or negatively charged surface groups occurring near undissociated –M–OH groups is different for oxides and hydroxides. pH corresponding to this state of the surface is called the **point of zero charge (PZC)**

4. Adsorption of immobile ions in one of the phases.

III.3. The Electrical Double Layer

An electrode becomes positively charged relative to the solution nearby if electrons leave it and decrease the local cation concentration in the solution. The most primitive model of the interface is that it is an electric double layer consisting of a sheet of positive charge at the surface of electrode and a sheet of negative charge next to it in the solution. A more detailed picture of the interface can be constructed by speculating about the arrangement of ions and electric dipoles in the solution. The **Helmholtz model** of the double layer assumes that the hydrated ions range themselves along the surface of the electrode but are held away from it by the molecules in their hydration spheres. The location of the sheet of ionic charge, which is called the outer Helmholtz plane, is identified as the plane running through the hydrated ions.

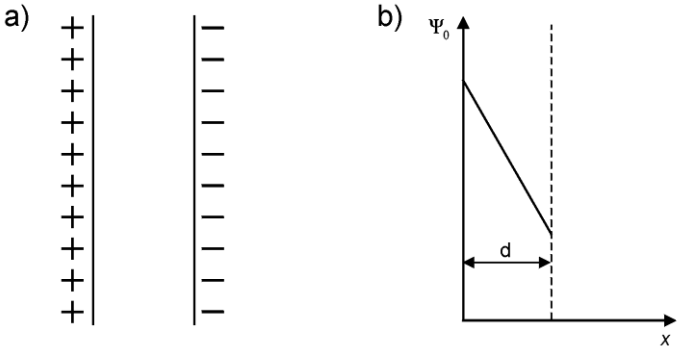


Fig. 1. Electric double layer scheme by Helmholtz:
a) charge distribution; b) distribution of potential in the distance function.

The Helmholtz model ignores the disrupting effect of thermal motion which tends to break up and disperse the rigid wall of charge. In the **Gouy-Chapman model** of the diffuse double layer the stirring effect of thermal motion is taken into account in much the same way as in the Debye-Hückel model of the ionic atmosphere of an ion with the latter's single central ion replaced by an infinite, plane electrode. **Fig. 1** shows the local concentrations in the Goy-Chapman model. As expected, ions of opposite charge cluster close to the electrode, and ions of the same charge are repelled from it. The modification of the local concentration near an electrode implies that it might be misleading to use activity coefficients characteristic of the bulk to discuss the thermodynamic properties of ions near the interface. Neither the Helmholtz nor the Goy-Chapman model is a very good representation of the structure of double layer. The former overemphasis the rigidity of the local solution, the latter underemphasizes its structure. The two are combined in the **Stern model**, in which the ions closest to the electrode are constrained into a rigid Helmholtz plane while outside that plane the ions are dispersed as in the Gouy-Chapman model.

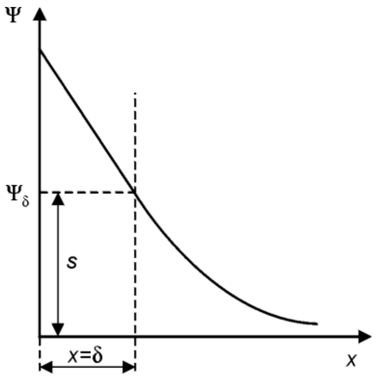


Fig. 2. Potential distribution in the electrical double layer by Helmholtz, Gouy and Chapman models.

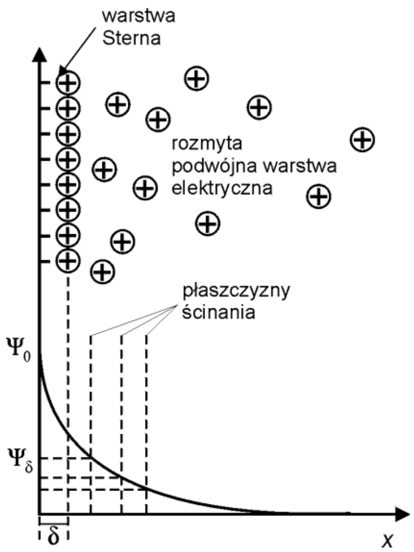


Fig. 3. Structure of electric double layer by Stern
and potential decreasing as the distance function from the interface

III. 5. Electrokinetic effects

When the relative movement of both phases is caused: charged surface and bulk phase, there can be observed the electrokinetic effects:

1. electrophoresis,
2. electroosmosis,
3. streaming potential,
4. sedimentation potential.

For determination of ζ potential one of the electrokinetic effects can be used. In electrophoresis and electroosmosis methods a specified electric field is introduced and mechanical properties are measured.

III. 6. Parameters characterising electrical double layer.

For electrical double layer characterization the following parameters are used based on the classical theories:

- surface charge and potential,
- external (diffusion) layer charge and potential,
- capacity of interior (C_1) and (C_2) exterior areas of electrical double layer – compact layer.
- For electrical double layer characterization two parameters are important:
- point zero of charge (PZC),
- isoelectric point (IEP).

According to the IUPAC definition:

PZC is the value of the negative decimal logarithm of the activity of the potential-determining ion in the bulk fluid ($\sigma_o = 0$ i $\psi_o = 0$).

For example, the charge on the surface of silver iodide crystals may be determined by the concentration of iodide ions in the solution above the crystals. Then, the PZC value of the AgI surface will be described by the concentration of I^- in the solution (or negative decimal logarithm of this concentration, pI^-).

IEP is the pH at which a particular molecule or surface carries no net electrical charge ($\zeta = 0$).

III. 7. Point of zero charge

The point of zero charge (PZC) in physical chemistry, is a concept related to the phenomenon of adsorption, and it describes the condition when the electrical charge density on a surface is zero. It is usually determined in relation to an electrolyte's pH, and the PZC value is assigned to a given substrate or colloidal particle. In other words, PZC is the pH value at which a solid submerged in an electrolyte exhibits zero net electrical charge on the surface.
The value of pH is used to describe PZC only for the systems in which H+/OH- are the potential-determining ions. Generally, PZC is the value of the negative decimal logarithm of the activity of the potential-determining ion in the bulk fluid.

Table I. Extreme pH_{pzc} values for some oxides.

[G.A. Parks, *Chem. Rev*. 65, 177 (1965), P. Ney, *Zeta Potentiale und Flotierbarkeit von Mineralen*, Springer Berlin 1973]

Oxide	pH_{pzc}	Oxide	pH_{pzc}
WO_3	0.2	UO_2	5.8–6.6
Sb_2O_3	0.2	CdO	10.4
SiO_2	1.8	Cr_2O_3	7.0
TiO_2	4.0 (<7)	ZnO	9.2
MnO_2	4.2	ZrO_2	10–11
HgO	7.3	Al_2O_3	5.0–9.2
CuO	9.5	BeO	10.2
Sn_2O_2	7.3 (6.6)	ThO_2	9.3
Fe_2O_3	6.6; 8.2 (9.04)	MgO	12.4
NiO	10.3	La_2O_3	10.4 (12.4)

III. 8. Isoelectric point versus the point of zero charge

The terms isoelectric point (IEP) and point of zero charge (PZC) are often used interchangeably, although under certain circumstances, it may be productive to make the distinction.

In the systems in which H+/OH- are the interface potential-determining ions, the point of zero charge is given in terms of pH. The pH at which the surface exhibits a neutral net electrical charge is the point of zero charge at the surface. Electrokinetic phenomena generally measure zeta potential, and a zero zeta potential is interpreted as the point of zero net charge at the shear plane. This is termed the isoelectric point. Thus, the isoelectric point is the value of pH at which the colloidal particle remains stationary in an electrical field. The isoelectric point is expected to be somewhat different from the point of zero charge on the particle surface, but this difference is often ignored in practice for so-called pristine surfaces, i.e., surfaces with no specifically adsorbed positive or negative charges. In this context, specific adsorption is understood as adsorption occurring in a Stern layer or chemisorption. Thus, point of zero charge at the surface is taken as equal to the isoelectric point in the absence of specific adsorption on that surface.

According to Jolivet [1], in the absence of positive or negative charges, the surface is best described by the point of zero charge. If positive and negative charges are both present in equal amounts, then this is the isoelectric point. Thus, the PZC refers to the absence of any type of surface charge, while the IEP refers to a state of neutral net surface charge. The difference between the two, therefore, is the quantity of charged sites at the point of net zero charge. Jolivet uses the intrinsic surface equilibrium constants, pK- and pK+ to define the two conditions in terms of the relative number of charged sites:

$$pK^{-} - pK^{+} = \Delta pK = \log \frac{[MOH]^{2}}{\left[MOH_{2}^{+}\right][MO^{-}]}$$

For large ΔpK (>4 according to Jolivet), the predominate species is MOH while there are relatively few charged species - so the PZC is relevant. For small values of ΔpK, there are many charged species in approximately equal numbers, which constitutes IEP.

III. 9. Methods of point of zero charge determination

III. 9. 1. Ahmed’s method

The easiest method of point of zero charge determination is the one where the solid with strongly expanded surface is added to the solution with simultaneous pH measurements. Then pH after the solid addition does not change, this point is the surface PZC point.

Practically, in this method a series of solutions with the same composition but with different pH values should be prepared. Differences in pH (ΔpH) after the addition of carefully defined amount of the studied substances of solid can be plotted on the graph:

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[1] Jolivet J.P., *Metal Oxide Chemistry and Synthesis. From Solution to Solid State*, John Wiley & Sons Ltd. 2000,ISBN 0-471-97056-5 (English translation of the original French text, *De la Solution à l'Oxyde*, InterEditions et CNRS Editions, Paris, 1994).

$$\Delta pH = f(pH_r)$$

Where: pH_r is pH of dispersion in equlibrium (terminal, equilibrium value of pH) and o the point of zero charge substance can be read from it.

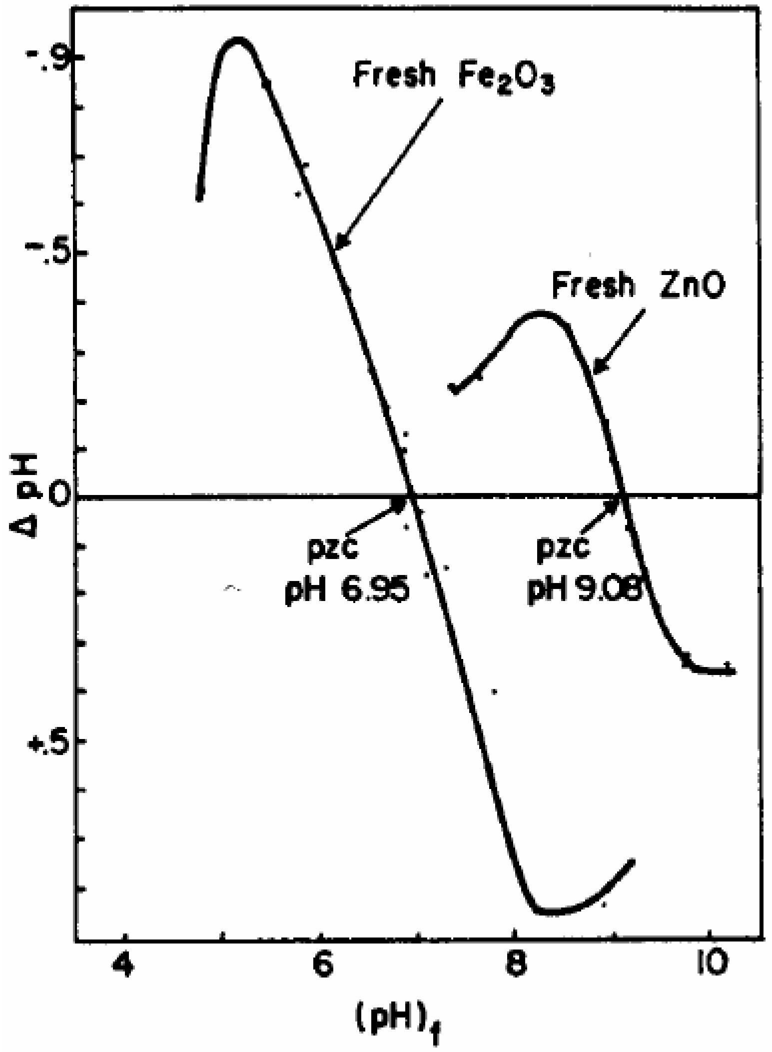

Fig. 5. PZC determination from ΔpH for Fe_2O_3 (electrolyte – KNO_3 solution) and ZnO (electrolyte – NaCl solution)
[A.L. Mular, R.B. Roberts, Trans. CIM 69, 438 (1966)]

III. 9. 2. Potentiometric titration method

Dispersion potentiometric titration is the most often used method for determination of point of zero charge and isoelectric point in the metal oxide/elctrolyte solution systems. In this method adsorption of potential-forming ions on the surface of solid phase is used.

In the first titration the dependence between the pH and the amount of the added acid or base is determined. The second titration solution contains some amount of solid.

Comparison of the titration curve allows to define PZC, which is in point of curves intersection.

Surface charge density is defined from the difference between the volume of acid or base added to obtain a defined value of pH:

$$\sigma_0 = \frac{\Delta VcF}{mS_w}$$

Where: $\Delta V = (V_s - V_e)$ - the difference between the volume of acid or base which is added to obtain a given value of *e* electrolyte and *s* suspension pH, *F* – the Faraday constant, *c* – the acid or base concentration, S_w – the oxide specific surface, *m* – oxide weight.

Surface charge can be also determined from the comparison of change of hydrogen or hydroxyl ions concentration in a given acid or base volume. The change can be calculated using the equation:

$$\sigma = \frac{V_e F\left(10^{pH_e} - 10^{pH_s} - 10^{-14+pH_s}\right)}{S_w m \gamma^{\pm}}$$

Where: $pH_e - the\ pH$ electrolyte solution, $pH_s - the\ pH$ suspension, V_e – the electrolyte volume (suspension), $\gamma^{\pm}$ - the activity coefficient

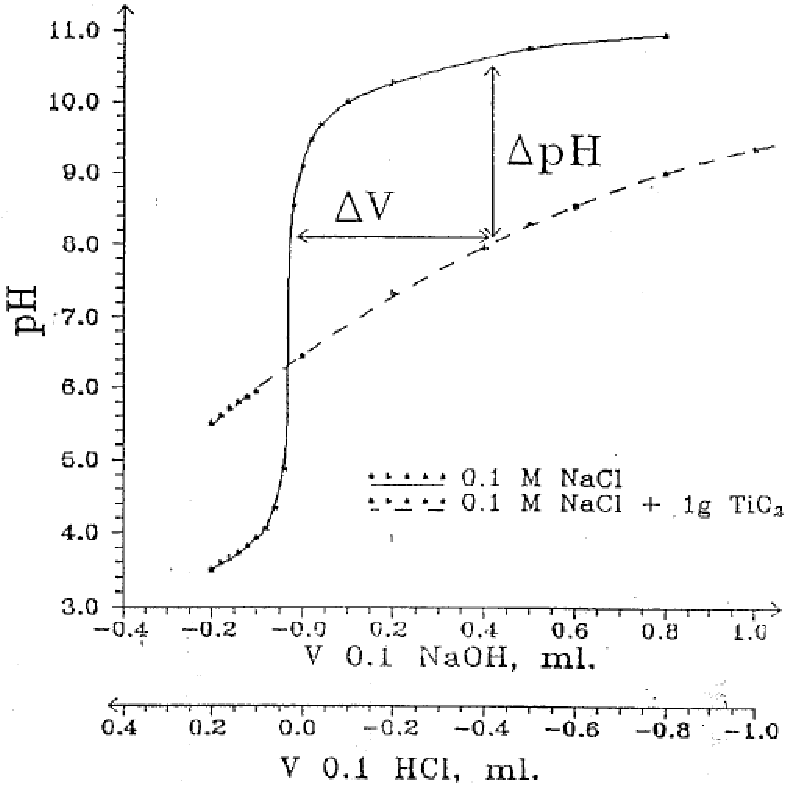

Fig. 6. Carrying electrolyte and suspension (TiO_2) titration curves [W. Janusz, „*Interfacial Forces and Fields, Theory and Applications*”, V. 85, Ch. 4, str. 135 (1999)].

III. 9. 3. Suspensive effect method (Palman's effect)

This suspensive effect method is based on the phenomenon of different activity of H^+ ions measured in sediment and clear liquid over the sediment layers.

$$\Delta pH = pH_{suspension} - \Delta pH_{solution}$$

When there is no difference between pH measured in sediment and under sediment, this solid is in PZC. Fig. 7 shows determination of PZC for ZnO using the potentiometric titration and measure of ΔpH. From the titration point $\Gamma_{OH^+} - \Gamma_{OH^-} = 0$ was obtained at pH=9.3, whereas ΔpH from the Palman's effect was pH=9.8.

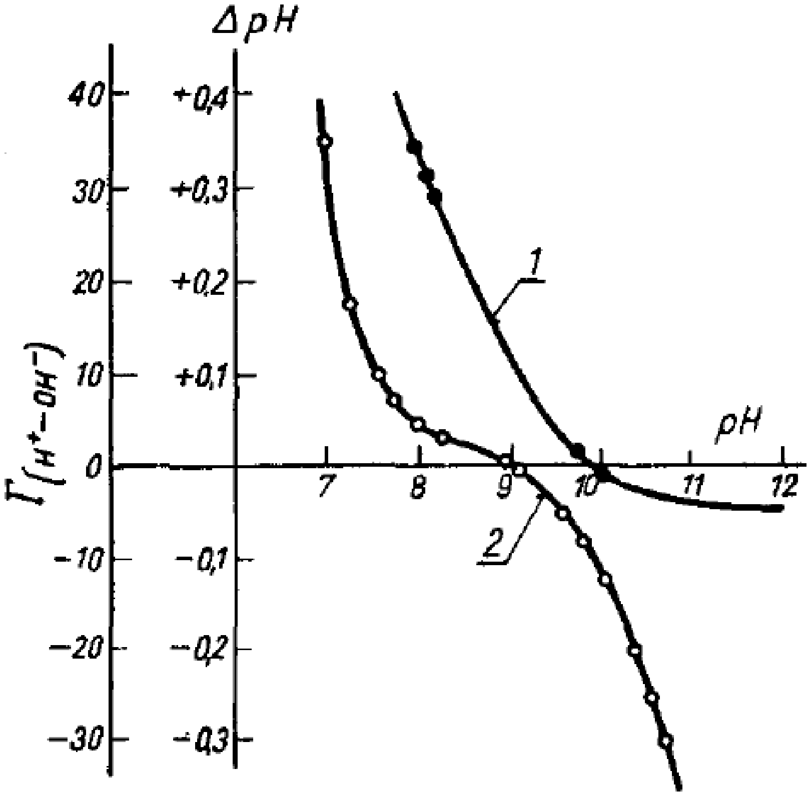

Fig. 7. Point of zero charge for ZnO measurement by different methods: 1 – the Palman's effect, 2- the potentiometric titration.
[J. Laskowski, Chemia fizyczna w procesach mechanicznej przeróbki kopalin, Wyd. Slask, Katowice 1969, str. 139].

IV. Experimental part

A. Apparatus and reagents

1. Apparatus: pH-meter CP-501, combined electrode , magnetic stirrer.
2. Equipment:
   - calibrated flask, 500 cm^3 – 1 piece,
   - polymer vessels volume, 100 cm^3 with lids– 6 pieces,
   - calibrated pipette volume, 50 cm^3 – 1 piece,
   - polymer pipettes – 2 pieces,
   - beaker volume, 100 cm^3 – 1 piece,
   - spraying vessel.
3. Reagents:
   - KCl stock solution, concentration 0.1 M,
   - neutral alumina oxide (0.063–0.2 mm),
   - KOH solution concentration 0.1 M and 0.02 M,
   - HCl solution concentration 0.05 M,
   - standard buffet solutions pH = 4.7 and 10,
   - distilled water.

B. Tasks program

1. pH-meter calibration.
2. Preparation of KCl solutions with proper pH.
3. Alumina oxide samples preparation.
4. Measurement of pH value of alumina oxide suspensions after the equilibrium state.

C. Apparatus operation

A pH-meter CP-501 is used for accurate measurements of pH, redox potential and temperature. With the electrode measurements of pH of water, solutions, gutters, suspensions, soils etc. are possible. Five point calibration is possible. Buffers pH value is automatically detected and this value can be changed by the user. Temperature corrections for pH value are automatic, and compatible with national standards. Membrane condition is evaluated automatically.

Calibration of pH-meter CP-501 with automatic temperature compensation

Rys. 10. pH-meter CP-501.

1. Turn on pH-meter **ON**.
2. Insert the combined electrode and temperature sensor into the vessel with buffer, pH 4.
3. Press button **CAL** and hold till symbol CAL blinks in the left side of light crystal display.
4. Press for a short time the button **CAL** and wait for establishment of pH value.
5. Take out the electrode and temperature sensor, rinse with distilled water and gently dry using filter paper.
6. Insert the electrode and temperature sensor into the vessel with buffer, pH 10.
7. Press shortly button **CAL** and wait for settlement of pH value.
8. Press the button **pH** to change the calibration course for the measurement course (blinking symbol CAL will disappear)
9. The apparatus is calibrated now and ready for measurements.

D. Method of doing the task

The calibrated 500 cm^3 flask prepare KCl solution of 0.01 M concentration from standard 0.1 M solution concentration. Next measure of 50 cm^3 of KCl for each of six polymer vessels. Adding HCl or NaOH solution (with proper concentration) establish pH of KCl solutions to about **4, 5, 6, 7, 9** and **10**.

To obtain the demanded value of pH some droplets of 0.05 M HCl (pH 4 or 5) or 0.02 M KOH (pH 6 or 7) or 0.1 M KOH (pH 9 or 10) should be added to KCl solution using a plastic pipette. After adding each droplet of acid or base, the solution should be mixed thoroughly using a magnetic stirrer. After stirring pH should be measured. Repeat this procedure until you obtain the required pH value. Write down the initial values of pH_0, of KCl solutions.

Due to small amounts of HCl and KOH added concentrations of KCl solutions do not change. After each pH measurement the electrode should be wiped.

pH measurement should be conducted with the magnetic stirrer ***turn down****.*
(not to damage the electrode).

Weigh 6 samples of 0.5 g neutral aluminum oxide. Add them to KCl solutions with pH_0. Cover vessels, mix them and leave for 30 min. for equilibrium fixing (mix the vessels several times). Then measure pH of the obtained solutions, dipping the electrode in the vessel under sediment. Read the pH value from the pH-meter after 1 min. after electrode dipping. Repeat these measurements for other KCl solutions, writing down pH_r values.

E. Data elaboration

1. The obtained data should be given in a table:

Concentration KCl = ...		
pH_o	pH_r	$\Delta pH = pH_r - pH_o$

where: pH_r – the pH value of aluminum oxide in equilibrium

(last fixed value of pH) ,

pH_o – the initial pH value of KCl solution, for each pH_r determined.

2. Show graphically the dependence $\Delta pH = f(pH_r)$.
3. Find the value of pH_r, where $\Delta pH = 0$. On the graph this value of pH determines the aluminum oxide point of zero charge.