Task 2

SURFACE CHARGE AND POINT OF ZERO CHARGE OF OXIDE ADSORBENTS AND THEIR MIXTURES

I. Aim of the task

The purpose of this task is to estimate the point of zero charge and surface charge of silica and alumina oxides and their mixture using the potentiometric titration method.

II. Introduction

1.   Point of zero charge.
2.   Isoelectric point.
3.   Point of zero charge measurements.
4. SiO_2 and Al_2O_3 materials.

References:

1. M. Kosmulski "Surface charging and points of zero charge", Surfactant science series, vol. 145, CRC Press/Taylor & Francis Group, 2009.
2. M.A.F. Pyman, J.W. Bowden and A.M. Posner, Clay Minerals, 14 (1979) 87-92.

III. Theory

III. 1.Surface charge

On the surface of solid materials, metal oxides in particular, surface charge is generated in contact with polar liquid. The most important causes of the charge formation involve:

- the existence of some crystallographic imperfections on the surface layer of solid (e.g., lack of ion or isomorphic ion substitution within the crystal structure);
- adsorption of protons or other ions on the surface of solid from the solution;
- dissociation or hydrolysis of the surface groups in contact with liquid.

With regard to the synthetic silica and alumina minerals, surface complexation reactions are expected to be a dominant source of the surface charge formation (Eq. 5-8). The net total particle surface charge, σ_P, is defined quantitatively as follows:

$$\sigma_P = \sigma_O + \sigma_H + \sigma_{IS} + \sigma_{OS} \tag{1}$$

where:

- σ_O is the net permanent structural-charge density due to isomorphic substitutions,
- σ_H is the net proton surface charge density created by the difference between the moles of protons and hydroxide ions complexed by the surface functional groups,
- σ_{IS} is the net innersphere complex surface charge density resulting from the net total charge of ions (excluding H^+ and OH^-) bound into inner-sphere surface coordination,
- σ_{OS} is the net outer-sphere complex surface charge density resulting from the net total charge of ions (excluding H^+ and OH^-) bound into outer-sphere surface coordination.

If a particle possessing a charge ($\sigma_P \neq 0$) is immersed in the polar solution, it will be surrounded by the counter ions. The diffuse layer is created. Its charge density noted as, σ_D, is equal in magnitude and opposite in sign to σ_P.

$$\sigma_P = -\sigma_D \tag{2}$$

The diffuse layer components can move freely in solution according to the electrostatic gradients. However charged particle surface needs to be constantly balanced by the counter ions present in the solution (in the surface vicinity). The term **point of zero charge (PZC)** refers to the conditions at which sum of the positive and negative charges gathered or created on the particle surface is equal to zero. Mathematically it can be expressed that the surface charge density Δq is equal:

$$\Delta q = q^+ - q^- = \sigma_D + \sigma_{IS} + \sigma_{OS} \tag{3}$$

where:

- q^+ and q^- refer to the adsorbed cation and anion charge, respectively, in units of moles of charge per square meter (C/m^2).

The intrinsic surface charge density, σ_{IN}, represents components of surface charge developed from the mineral structure, which must be balanced by adsorption of ions from solution:

$$\sigma_{IN} = \sigma_O + \sigma_H = -\Delta q \qquad (4)$$

The point of zero net charge (PZNC) is defined as the pH value where σH is equal to zero. Therefore, using equation 4, this is the pH value where $\Delta q = -$ σo. Experimental methods for measuring surface charge components from Eq. 4 include proton titration for σH, preferential Cs+ adsorption for σo and background ion adsorption for Δq. Whereas σo is constant for given material, σH and Δq vary with pH and ionic strength.

The value of pH is commonly used to describe PZC for the systems in which H+/OH- are the potential determining ions:

$$\equiv X - O - H \rightleftarrows \equiv X - O^- + H^+ \qquad (5)$$

$$\equiv X - [O_{-H}^{-H}]^+ \rightleftarrows \equiv X - O - H + H^+ \qquad (6)$$
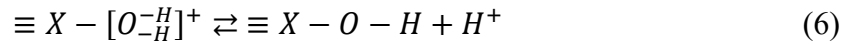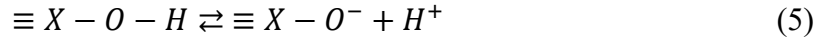
When pH is lower than the PZC value, the system is said to be "below the pzc", where the acidic solution donates more protons than hydroxide groups, and so the adsorbent surface is positively charged. Conversely, above the PZC the surface is negatively charged – see Fig. 1.
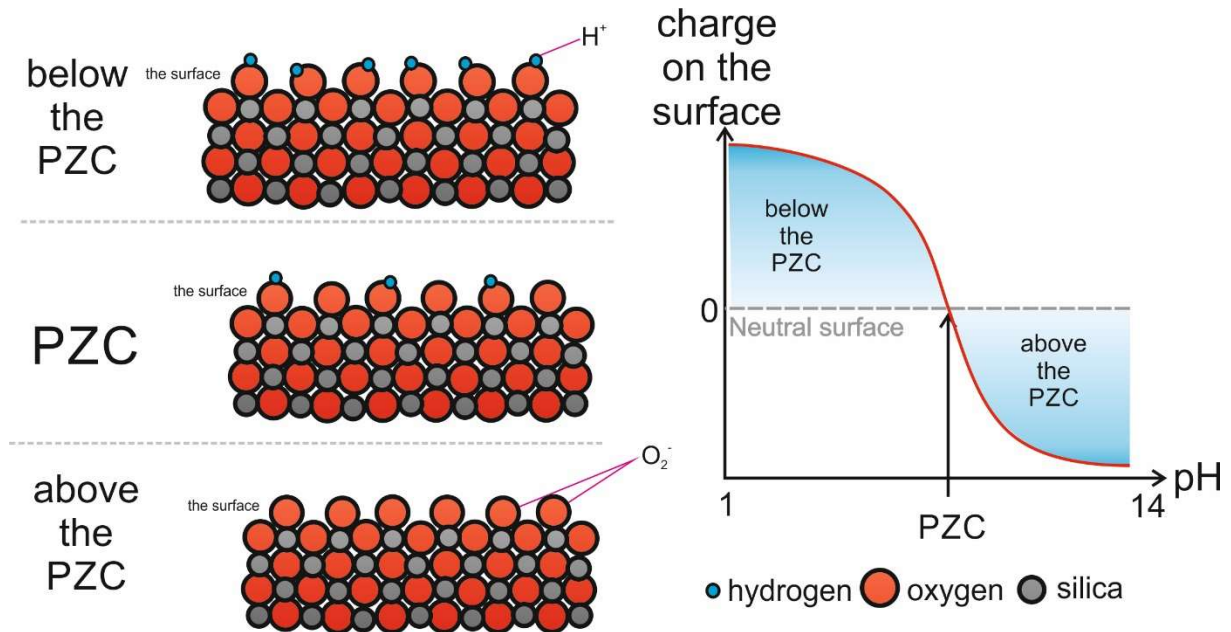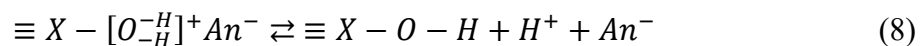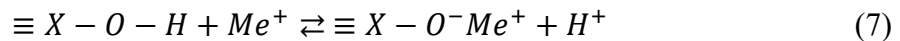

Fig. 1. Schematic representation of the point of zero charge (based on [1]).

Apart from hydrogen ions, electrolyte ions play a significant role in creating the surface charge. Cations (Me^+) and anions (An^-) present in the electrolyte may react with oxide surface hydroxyls creating complex fusions.

$$\equiv X - O - H + Me^+ \rightleftarrows \equiv X - O^- Me^+ + H^+ \qquad (7)$$

$$\equiv X - [O_{-H}^{-H}]^+ An^- \rightleftarrows \equiv X - O - H + H^+ + An^- \qquad (8)$$

The surface charge density is an algebraic sum of the group charges that were created in reactions 5 to 7.

$$\sigma_0 = B \times \{\equiv X - [O_{-H}^{-H}]^+ + \equiv X - [O_{-H}^{-H}]^+ An^- - \equiv X - O^- Me^+ - \equiv X - O^-\} \quad (9)$$

where: B is the coefficient of conversion.

The coefficient of conversion is equal to the ratio of the surface density expressed in mol/m^2 over the charge density expressed in C/m^2.

Point of zero charge is of fundamental importance in surface science and has countless applications in technology of colloids, e.g. flotation of minerals. At the PZC the colloidal system exhibits zero zeta potential (particles remain stationary in an electric field), minimum stability (exhibits maximum coagulation/flocculation rate), maximum solubility of the solid phase and maximum viscosity of the dispersion. Next to the PZC in the literature quite often when reading about surface properties of insoluble oxides one can encounter term: the isoelectric point. **The isoelectric point (IEP)** is defined as the conditions under which the electrokinetic charge density and thus the electrokinetic potential (ζ) equals zero. It can be determined by the electrokinetic methods such as electrophoresis, electroosmosis and also by electroacoustic method. The pH value of the solid dispersion at which the electrokinetic potential of the solid particles is equal to zero is known as pH_{IEP}. Equality between pH_{PZC} and pH_{IEP} exists only if no specific sorption of ions from the solution takes place nor permanent negative charge is present at the surface. Usually the PZC differs from the IEP and those two terms shouldn't be used interchangeably.

III. 2. The point of zero charge determination techniques

The techniques for the PZC determination are based on the assumption that protons and hydroxyl groups are potential-determining ions. The pH at which the surface has zero net charge, known as pH_{PZC}, is characteristic for amphoteric surfaces and is determined by the type of the surface sites on solids and their structure.

The point of zero charge may be estimated using the **suspension effect method** (Pallmann effect). The method relies on the differences in measured activities of protons in the sediment layer and in clear solution above the sediment. The solid surface has zero charge when the difference between the solution and the sediment does not exist ($\Delta pH = 0$):

$$\Delta pH = pH_{suspension} - pH_{electrolyte} \tag{10}$$

The most frequently used method of the pH_{PZC} estimation at the solid - liquid interface is a **potentiometric titration**. This method monitors pH changes in a function of titrant volume (acid or base) of the electrolyte and the suspension. Both systems needs to have the same ionic strength. The intersection point of potentiometric titration curves gives the PZC value – see Fig. 2.
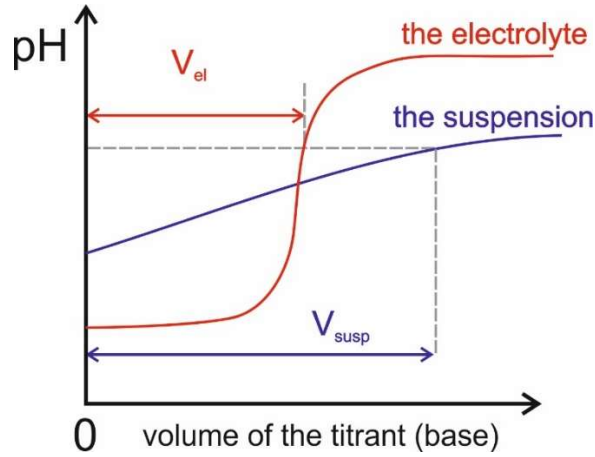
Fig. 2. Curves of titration of the background electrolyte and suspension.

The surface charge density can be calculated from the difference in volumes of added acid or base to obtain certain pH value of suspension using the equation:

$$\sigma_0 = \frac{\Delta V \times c \times F}{m \times S_w} \tag{11}$$

where:

- ΔV – the difference in volume of titrate necessary to obtain the appropriate pH value of electrolyte and suspension ($\Delta V = V_{suspension} - V_{electrolyte}$);
- F – the Faraday constant (96 485 $\left[\frac{sA}{mol}\right]$);
- c – the concentration of titrate $\left[\frac{mol}{dm^3}\right]$;
- S_w – the specific surface area of oxide $\left[\frac{m^2}{g}\right]$;
- m – the mass of oxide in suspension $[g]$.

The surface charge density can be also obtain by comparison of the pH values for the electrolyte and the suspension at given titrant amount:

$$\sigma_0 = \frac{V_e \times \left(10^{-p\ e-1}\ ^{-pH_s} - 10^{-14+p\ e} + 10^{-14+p\ s}\right)}{m \times S_w} \tag{12}$$

where:

- V_e – the volume of electrolyte;
- pH_e – the pH of the electrolyte solution;
- pH_s – the pH of the suspension.

However, because of the mathematical complexity, the equation 12 is not so often used for σ_0 estimation. The other methods based on the potentiometric titration relies on the estimation of **the common intersection point** (CIP) (see Fig. 3) or on the phenomenon of merging observed for curves obtained at three or more different ionic strengths.
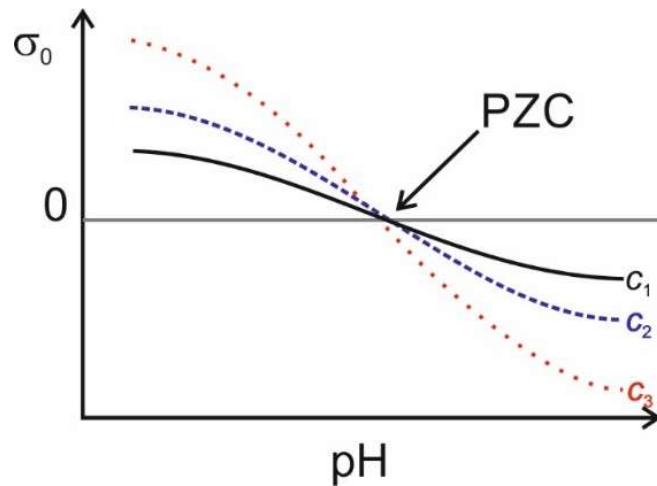
Fig. 3. Common intersection point (CIP) at the PZC of potentiometric titration, $c_1<c_2<c_3$ (based on [2]).

The nature of titrate as well as the rate of titration significantly affect the PZC value – see Fig. 4.
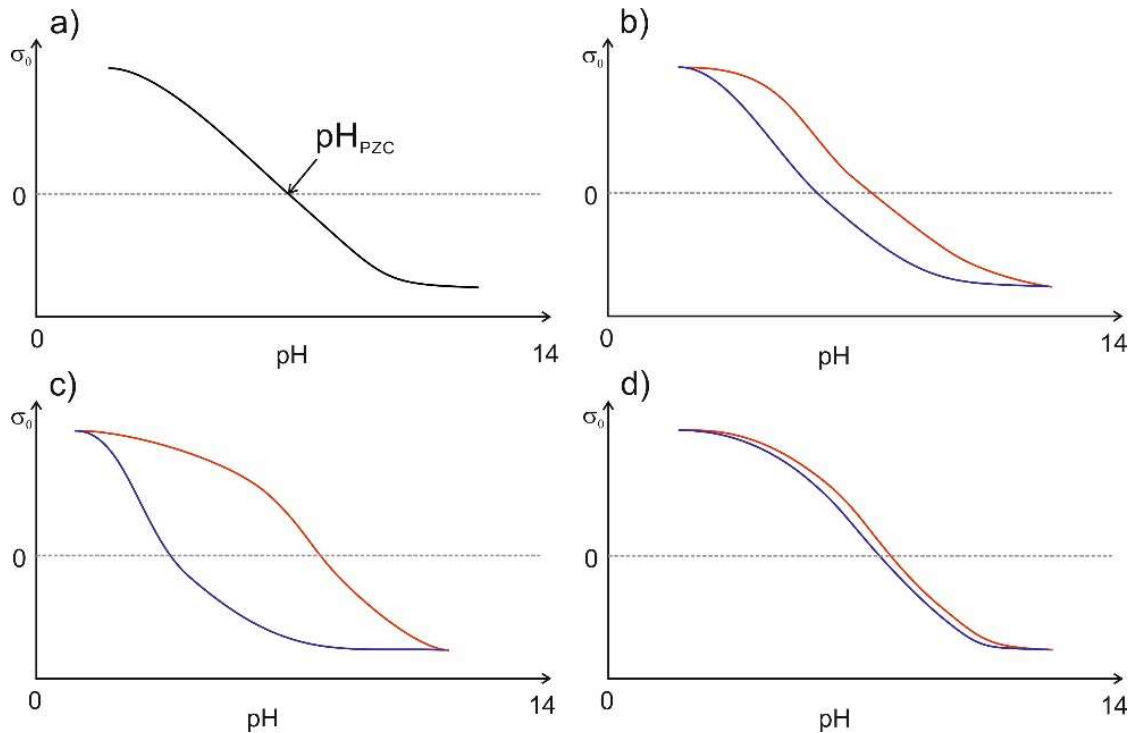

Fig. 4. Influence of titrate and velocity of titration on PZC (red line basic titration, blue line acidic titration): a) ideal situation (acidic and basic titration curves overlap) , b) real system (acidic and basic titration curves doesn't overlap – the created loop is called titration hysteresis), c) fast titration – hysteresis loop strongly affects estimated pHPZC, d) slow titration – negligible hysteresis (based on [2]).

The PZC is also affected by the temperature and the background electrolyte nature – see Table 1.

Table 1. Compilation of the experimental PZC values for Al_2O_3 and SiO_2 materials obtained at 25°C (based on [3]).

Material	Source of the material	Electrolyte	$C_{electrolyte}$ [mol/dm^3]	Method	pH
Al_2O_3	γ, Aerosil, purified	NaNO$_3$	0.001-0.1	CIP	8.3
	Fumed	NaCl	0.001	IEP	9.5
	α, CR6	NaCl	0.001-0.1	CIP	8.8
	α, Aldrich, heated at 700°C	NaCl	0.005	IEP	6.5
	α, 99,99% Showa Denko	NaNO$_3$	0.001	IEP	9.2
	Degusa C	KNO$_3$	0.005-0.5	CIP	8.0
SiO_2	Fumed	NaCl	0.001	IEP	2.2
	Ludox HS, DuPont	KCl	0.001	IEP	3.0
	From sodium silicate	NaCl	0.001	IEP	2.3
	Quartz, Alfa Aesar	NaNO3	0.001-0.1	CIP	2.9
	Quartz, high purity, Bottley	KCl	0.001	IEP	3.0
	Klebosol	KCl	0.05	IEP	4.0
	Stober	KNO$_3$	0.01	IEP	2.9

Increase in the suspension temperature will result in the rise of the electrolyte ions activity and will decrease physical adsorption of ions on the surface of solid particles.

The nature rarely creates chemically pure minerals. Since PZC value is essential in many applications it is crucial to obtain its value for mechanically mixed oxide systems [4]. In case of a stoichiometric mixture of alumina ($m_{Al}[g]$) and silica ($m_{Si}[g]$) it is expected that at the PZC negative charge developed on the Al_2O_3 will be equal to positive charge on the SiO_2. Thus, at the constant ionic strength, the relation between the weight percent composition $\left(\frac{m_{Si}}{m_{Al}+m_{Si}}\right)$ and surface charge of both oxides σ_{Si}, σ_{Al} expressed in C/g is as follows:

$$\sigma_{Al}\left(\frac{m_{Al}}{m_{Al}+m_{Si}}\right) + \sigma_{Si}\left(\frac{m_{Si}}{m_{Al}+m_{Si}}\right) = 0 \qquad (13)$$

In the calculations values σ_{Si}, σ_{Al} can be obtained from the experiments with pure oxide materials.

III. 2. Silicon and aluminum oxides

Silicates are the oxides of silica, where the Si atom shows tetrahedral coordination, with four oxygen atoms surrounding the central Si atom – see Fig. 5.
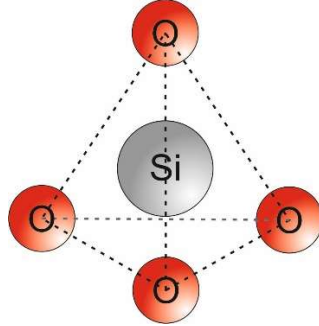

Fig. 5. Tetrahedral structural unit of silica.

In each of the thermodynamically stable forms of silica all of oxygen atoms of the SiO_4 tetrahedra are shared with others, yielding the net chemical formula: SiO_2. Silicon dioxide occurs in both crystalline (e.g. quartz, tridimite, cristobalite, faujasite, coesite, stishovite, moganite) and amorphous forms (i.e., forms are amorphous on the 1nm length scale, Fig. 6).

Amorphous silica dioxide consists of randomly linked spheroidal polymerized silicate particles, i.e., the primary particles, which in turn are built up from SiO_4 tetrahedra with variable Si-O-Si bond angles and Si-O bond distances. The properties of silica gels results from the state of aggregation of the primary particles and the chemistry of their surfaces. The surface area, porosity and surface chemistry can be controlled during the production process.
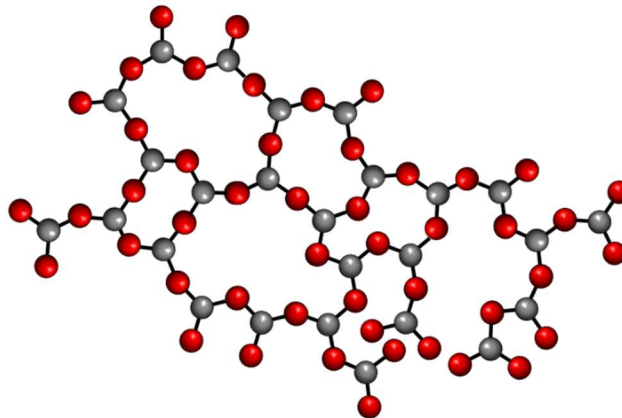

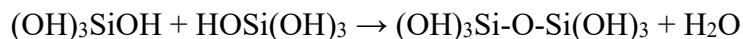**Fig. 6.** The amorphous structure of silica gel (for the clarity some oxygen atoms behind the plane of the picture and in front of it are omitted).

Silica gels are fabricated in the sol-gel process as a result of polycondensation of orthosilicic acid:

$$(OH)_3SiOH + HOSi(OH)_3 \rightarrow (OH)_3Si\text{-}O\text{-}Si(OH)_3 + H_2O$$

The reaction leads to creation of the silicilic acid macroparticles by proceeding through three stages:

1) **Polymerization** of monomers to form small primary particles;
2) **Growth** of primary particles;
3) **Linking** of particles into branched chains, networks and finally gel.

As a result, the silica particles surface is covered by the SiOH groups. The nature of the silica surface and its interactions with various reactants were extensively studied in 1960s and 1970s. Frim them it follows that different types of hydroxyl groups are present on the silica surface which determine various surface phenomena. 7.
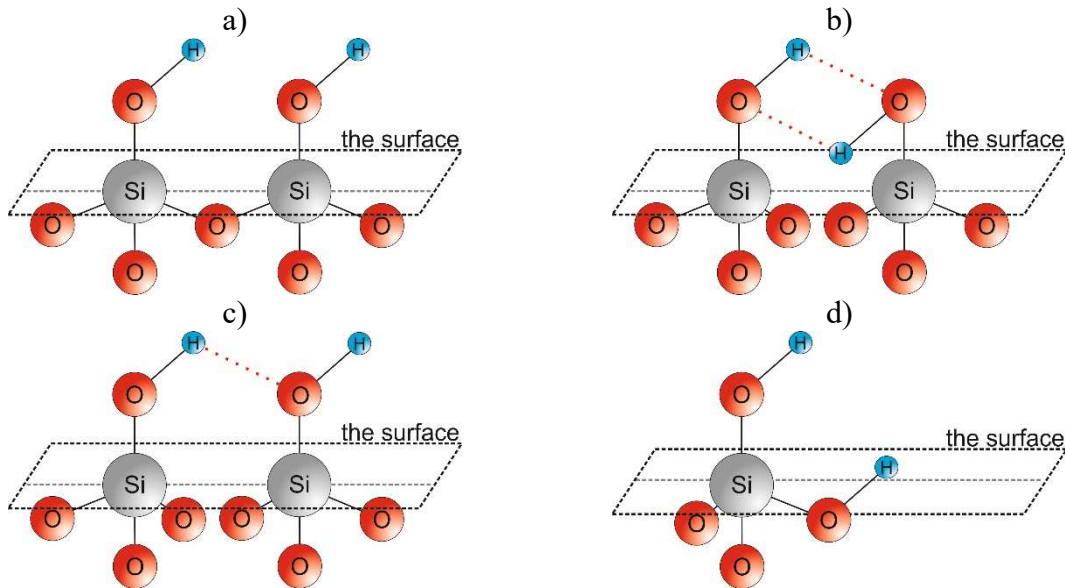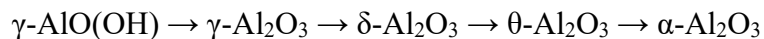

Fig. 7. Types of hydroxyl groups on the surface of silica gel distinguished by Snyder:
a) single (isolated); b) hydrogen bonded; c) active; d) double (germinal) (based on [5]).

The surface properties such as (pore volume, pore size distribution and specific surface area) of the amorphous silica gel can be characterize by the low temperature nitrogen adsorption/desorption experiment and is presented in Task 1A.

Alumina (Al_2O_3) is mainly obtained by dehydratation of various aluminum hydroxides (e.g bohemite). The bohemite which main component is γ-AlO(OH), decomposes and transforms gradually through different crystallographic forms of alumina into thermodynamically most stable form of α-Al_2O_3:

$$\gamma\text{-AlO(OH)} \rightarrow \gamma\text{-Al}_2\text{O}_3 \rightarrow \delta\text{-Al}_2\text{O}_3 \rightarrow \theta\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$$

The first systematic classification of alumina was proposed by Ginsberg et al. [6] and was subsequently modified by Lippens [7]. It is based on the temperature ranges in which alumina is obtained from hydroxides. Group γ comprises low-temperature aluminum oxides ($Al_2O_3 \cdot x$ H_2O, where: x = 0 to 0.6) obtained at temperatures below 600°C. This group includes ρ-, χ-, η- and γ-aluminum oxides. Group δ includes high temperature aluminum oxides (practically anhydrous Al_2O_3) obtained at the temperatures ranging from 900°C to 1000°C. This group includes κ-, θ- and δ-aluminum oxides. At a temperature 1200°C and higher octahedral α-alumina oxide is obtained [8].

The form of alumina most commonly used as an adsorbent is γ-Al_2O_3, with the specific surface area of 100-200 m^2/g. Its surface is built of O_2^- and Al^{3+} ions, with only ¾ of the positions specific for alumina being occupied.

Alumina may contain different quantities of surface hydroxyls or adsorbed water. Moreover, in addition to regular, cylindrical micropores, their structure exhibits irregular pores of larger diameters [8].

References to the *Theory*

[1] L. Bruce Railsback "Some Fundamentals of Mineralogy and Geochemistry":

www.gly.uga.edu/railsback/FundamentalsIndex.html

[2] M. Kosmulski " Surface charging and points of zero charge", Surfactant science

series, vol. 145, CRC Press/Taylor & Francis Group, 2009.

[3] M. Kosmulski, Journal of Colloid and Interface Science, 298 (2006) 730–741.

[4] M.A.F. Pyman, J.W. Bowden and A.M. Posner, Clay Minerals, 14 (1979) 87-92.

[5] L.R. Snyder, Principles of Adsorption Chromatography, Marcel Dekker Inc., New York – London, 1968.

[6] H. Ginsberg, W. Hüttig, G. Strunk-Lichtenberg, Z. anorg. Allgem. Chem. 293 (1957) 204.

[7] B.C. Lippens, Structure and Texture of Aluminas, Thesis, Delft Univ. of Technology, The Netherlands, 1961.

[8] J. Ościk, "Adsorption", Ellis Horwood Limited, Publishers – Chichester, 1979.

IV. Experimental

A. Equipment and reagents

1. Instrumentation:
- Multifunction meter CX-401 ELMETRON.

2. Equipment:
- 3 polypropylene vessels (60 mL);
- Glass pipette (0.1 ml);
- Measuring cylinder (50 ml).

3. Reagents:
- Electrolyte: 0.1 M NaCl water solution (with the addition of HCl);
- 0.1 M NaOH water solution;
- Buffer solutions of pH equal to 4, 7 and 10;
- Al_2O_3 (neutral);
- SiO_2.

B. Preprataion of the CX-401 ELMETRON for the measureaments

The multifunction meter CX-401 ELMETRON is shown in the picture on the right.

1) To turn on the pH-meter press and shortly hold FUNCTION button.

2) By pressing FUNCTION button switch to pH measurements. When pressing FUNCTION take notice that frame at the bottom of the display changes through different device functions.

3) By pressing 3 times MODE set P.CAL on the display. If you by accident skip P.CAL don't worry just keep pressing MODE until you reach it again.

4) Using arrows on the device panel set Ust.

5) At this moment by shortly pressing CAL you can check values of the five calibration buffer solutions named P1, P2… etc. in the device memory. If your buffers have different values than those in the device you can use arrows to adjust pH in every calibration solution.

6) When pH values are set, press FUNCTION button.
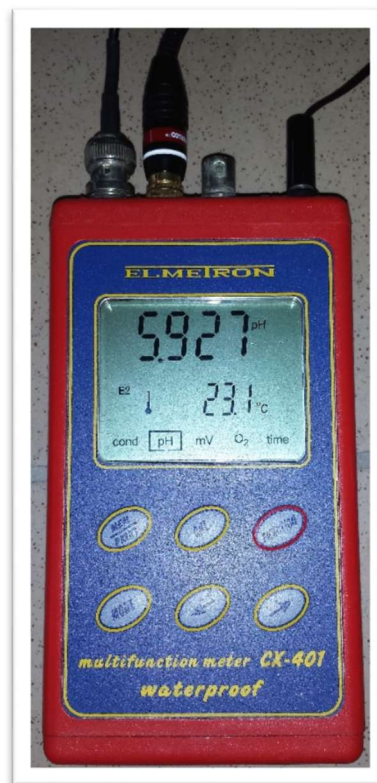
7) **The Calibration.**

8) Press and hold for 3s CAL button. On the display sign 'CAL' will appear.

9) Rinse thoroughly with distilled water the electrode and the TP. Except the electrode glass bulb, wipe the electrode and the TP with paper towel. The glass bulb of the electrode should be carefully dabbed (lightly touched with paper towel), not wiped.

10) Immerse the electrode and the TP into the pH=4 buffer. Make sure that the porous frit on the electrode is immersed in the solution. P2 symbol will appear on the display.

11) Wait for at least 3 min. and press shortly CAL button. The pH value will blink several times and will change to pH= 4.000.

12) Repeat points from 8-10 with pH=7 and pH=9 buffered solutions. During the calibration P3 and P4 symbols will appear respectively.

13) Press FUNCTION button. The calibration is complete and the multifunction meter CX-401 ELMETRON is ready for the pH measurements. Proceed with the measurements.

C. The execution of exercise

1) Dispense into each polypropylene vessel 50 mL of the electrolyte solution (1 M NaCl)
2) First sample (E) is ready.
3) Add 1 g of Al_2O_3 to the second container and stir for 10 s (1S).
4) Add mixture of 0.7 g of alumina and 0.3 g of silica to the third container and stir for 10 s (2S).
5) Measure the pH of the E, 1S & 2S systems (in case of suspensions wait until oxide particles will settle at the bottom of the container). The pH value should be read when CX-401 ELMETRON displays stable pH value or after 10 min. of electrode immersion in the system.
6) Afterwards, add 0.05 mL of 0.1 M NaOH solution to each system (E, 1S & 2S) and stir for 10 s. Measure the pH.
7) Repeat procedure from point 5-6.
8) Collect data in the Table 2.

Table 2.

V_{NaOH} [ml]	pH_E	pH_{1S}	pH_{2S}
0.00			
0.05			
0.10			
0.15			
0.20			
0.25			
0.30			
0.35			
0.40			
0.45			

D. Analysis of the results

In one figure draw plots $pH = f(V)$ for each investigated system. Estimate the point of zero charge for Al_2O_3 and for mixture of oxides. Using equations (11) and (13) calculate surface charge of Al_2O_3 and SiO_2 in the mixture at the PZC. (Take into account converting the surface charge units from C/g into C/m^2). Take useful parameters from the specifications of nitrogen adsorption/desorption from Al_2O_3 and SiO_2 (see the next two pages).

Micromeritics Instrument Corporation
ASAP 2405N V1.01   ADSORBATE: NITROGEN

SAMPLE DIRECTORY/NUMBER: DATA8   /178   START 12:23:03 07/07/06
SAMPLE ID: SiO₂   COMPL 04:40:01 07/08/06
 SUBMITTER: REPRT 14:02:43 07/11/06
OPERATOR: SAMPLE WT: 0.3335 g
STATION NUMBER: 1 EQUIL INTERVAL: 10 sec FREE SPACE: 92.3843 cc

SUMMARY REPORT

AREA

BET SURFACE AREA: 313.8476   sq. m/g

LANGMUIR SURFACE AREA: 400.1624   sq. m/g

SINGLE POINT SURFACE AREA AT P/Po 0.1964: 305.7672   sq. m/g

BJH CUMULATIVE ADSORPTION SURFACE AREA OF PORES
BETWEEN 17.0000 AND 3000.0000 A DIAMETER: 350.2673   sq. m/g

BJH CUMULATIVE DESORPTION SURFACE AREA OF PORES
BETWEEN 17.0000 AND 3000.0000 A DIAMETER: 415.8931   sq. m/g

MICROPORE AREA: 25.9297   sq. m/g

VOLUME

SINGLE POINT TOTAL PORE VOLUME OF PORES LESS THAN
2449.8213 A DIAMETER AT P/Po 0.9921:   1.277959 cc/g

BJH CUMULATIVE ADSORPTION PORE VOLUME OF PORES
BETWEEN   17.0000 AND   3000.0000 A DIAMETER: 1.286904 cc/g

BJH CUMULATIVE DESORPTION PORE VOLUME OF PORES
BETWEEN   17.0000 AND   3000.0000 A DIAMETER: 1.278683 cc/g

MICROPORE VOLUME: 0.010409 cc/g

PORE SIZE

AVERAGE PORE DIAMETER (4V/A BY BET):   162.8763   A

BJH ADSORPTION AVERAGE PORE DIAMETER (4V/A): 146.9625   A

BJH DESORPTION AVERAGE PORE DIAMETER (4V/A): 122.9819   A

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                       Micromeritics Instrument Corporation
ASAP 2405N V                                ADSORBATE: NITROGEN

SAMPLE DIRECTORY/NUMBER: DATA14  /233     START 10:08:02 03/24/09
SAMPLE ID: Al₂O₃                          COMPL 18:32:57 03/24/09
SUBMITTER:                                REPRT 08:08:46 03/25/09
OPERATOR:                                 SAMPLE WT:    0.8465 g
STATION NUMBER: 1   EQUIL INTERVAL: 5 sec  FREE SPACE:  93.4453 cc
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SUMMARY REPORT

AREA

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BET SURFACE AREA:                          128.2239   sq. m/g

LANGMUIR SURFACE AREA:                     162.4520   sq. m/g

SINGLE POINT SURFACE AREA AT P/Po 0.1945:  125.7371   sq. m/g

BJH CUMULATIVE ADSORPTION SURFACE AREA OF PORES
  BETWEEN    17.0000 AND   3000.0000 A  DIAMETER: 165.1519   sq. m/g

BJH CUMULATIVE DESORPTION SURFACE AREA OF PORES
  BETWEEN    17.0000 AND   3000.0000 A  DIAMETER: 192.4010   sq. m/g

MICROPORE AREA:                              1.3106   sq. m/g
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VOLUME

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SINGLE POINT TOTAL PORE VOLUME OF PORES LESS THAN
     921.4639 A  DIAMETER AT P/Po 0.9785:       0.262623 cc/g

BJH CUMULATIVE ADSORPTION PORE VOLUME OF PORES
  BETWEEN    17.0000 AND   3000.0000 A  DIAMETER:   0.271571 cc/g

BJH CUMULATIVE DESORPTION PORE VOLUME OF PORES
  BETWEEN    17.0000 AND   3000.0000 A  DIAMETER:   0.265132 cc/g

MICROPORE VOLUME:                                 0.000675 cc/g
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PORE SIZE

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AVERAGE PORE DIAMETER (4V/A BY BET):        81.9263   A

BJH ADSORPTION AVERAGE PORE DIAMETER (4V/A):  65.7748   A

BJH DESORPTION AVERAGE PORE DIAMETER (4V/A):  55.1206   A
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