



Laser-Induced Current Transient Technique

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Physics of Energy Conversion and Storage

Things to note before the lab course

1. Please read the following introduction (**section 1**) and safety instruction (**section 6**) carefully.
2. For this lab course, EC-lab and Origin apps are required to analyze the obtained data.
3. You need to write down what the lab demonstrator is telling to you. Because most of them are important to your report.

1. Introduction

1.1 Electric Double Layer

The theory of the Electric Double Layer (EDL) was first published by Hermann L.F. von Helmholtz to explain the potential and charge arrangement existing at the interface between an electrode (electron conductor) and an electrolyte (ionic conductor). When a potential is applied to the system, the structure of the charged metal electrode (q_M) and the solution (q_s) is a sort of capacitor. Then the equation can be expressed as:

$$q_M = -q_s$$

The charge at the metal surface is localized in the outer thin layer because of the high conductivity inside the metal, and its sign is opposite to the electrode surface charge. The Helmholtz layer model is considered the simplest one way to show the charge distribution. The plane consisting of the specifically adsorbed ions (**Figure 1.1**) is defined as the inner Helmholtz plane (IHP). The cations next to the electrode form a plane parallel to the electrode surface as shown in **Figure 1.1**. The plane is called the outer Helmholtz plane (OHP).¹

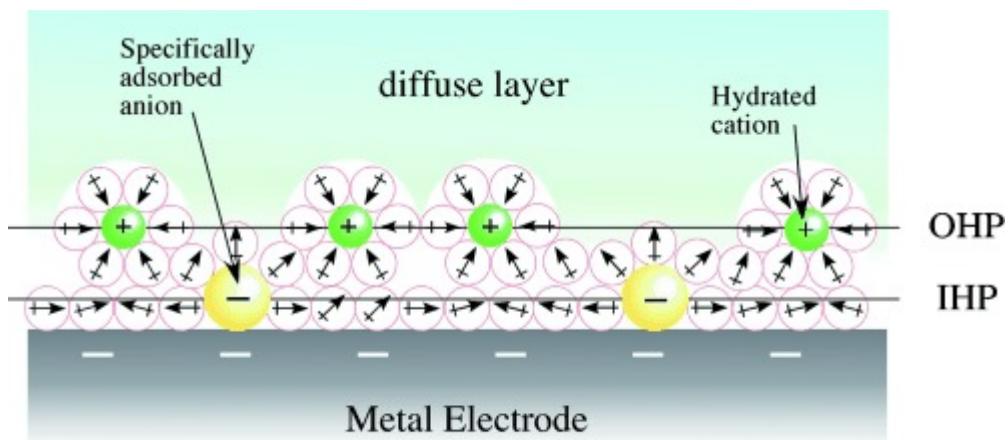


Figure 1.1. Model of the electric double layer on a metal electrode. The spheres with arrows designate water dipoles. The arrows indicate the direction of the water dipole.

1.2 Potential of Zero Charge and Potential of Maximum Entropy

The concept of potential of zero charge (PZC) was introduced in 1928. Then, PZC is considered as one of the most important parameters for understanding the interface between the electron conductor and ionic conductor. Based on EDL, electrode charge is defined as the charge of the (metal) electrode surface. In this case, the definition of PZC is a potential at which the electrode surface has no excess charge. For transition metals, the PZC related to their work function, which can be shown as:

$$E_{\text{PZC}} = \frac{\Phi}{e_0} + K$$

where Φ is the metal's work function, e_0 is the electron charge, and K is a constant, which depends on the influence of the solvent on the E_{PZC} of the given electrode.

Basically, the value of the PZC is influenced by the electrode materials, electrode surface structure and electrolyte composition.² However, one should involve adsorption processes in the electrode charge. Then two different values of PZC have to be considered:^{3,4,5}

1. The potential of zero free charge (PZFC) is a type of PZC of metal without adsorption processes.
2. The potential of zero total charge (PZTC), defined as a potential at which the sum of the free, electronic net charge density, as well as the charge density transferred during reversible adsorption processes, are zero.

In this case, these two values coincide for an ideally polarizable electrode because there is no charge transfer associated with adsorption. However, PZFC and PZTC are different for the Pt-group metal electrodes. Hence, in cases of the metals adsorbing hydrogen or oxygen, the PZTC exhibits a pH dependence.⁶ One should note that only the PZTC can be obtained experimentally and PZTC behaves a pH dependence because of hydrogen or oxygen adsorbed on metal surface.

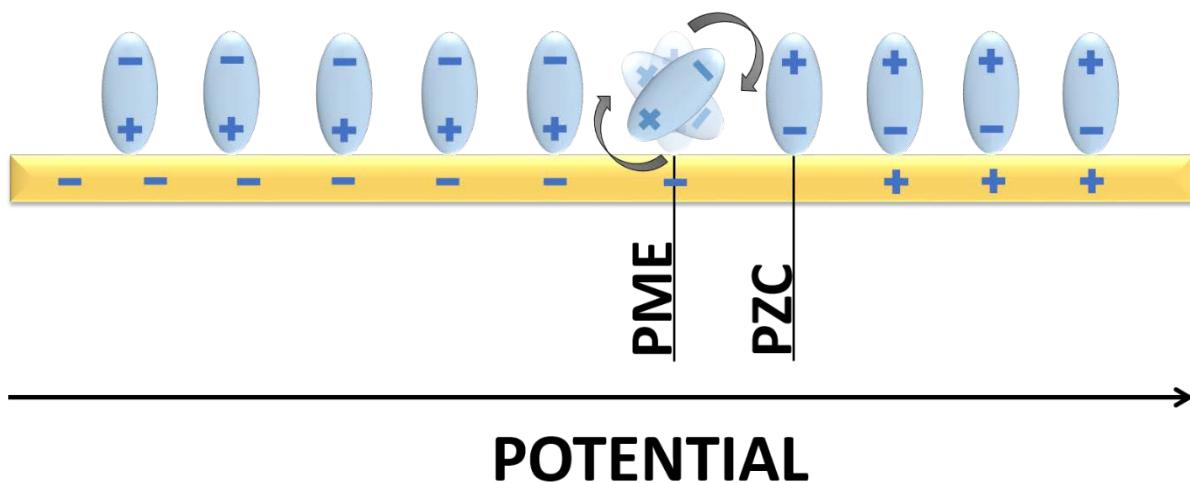


Figure 1.2. Simplified schematic of the water dipoles orientation toward the metal surface according to the surface charge in aqueous electrolytes. The potential at which there is a maximum disorder in the interfacial layer corresponds to the PME, while the PZC represents the potential at which the net surface charge equals zero. In most cases, the PZC and PME of metal electrodes are located close to each other⁷.

The potential of maximum entropy (PME), where the entropy of formation of the double layer is maximal is another parameter of paramount importance for the characterization of the above mentioned systemy systems. At the potential which closes to PME, there is maximum disorder of water layer at the electrode surface¹⁴. That means in the vicinity of PME, water molecule can re-orientate more easily, whereas the solvent structure is more rigid at potentials more remote from PME (see Figure 1.2.). In most case, the PME is closely related to the PZC. For instance, the PME for mercury or gold electrodes immersed in aqueous solutions has a slightly more negative value than the PZC. The difference of value between PZC and PME results from the specific interactions between water molecules and (uncharged) metal surfaces leading to the nearly flat orientation of the solvent dipoles at the surface.⁸ This is because of a strong directional bond formed between the oxygen atom and unoccupied d-orbitals at the metal surface.⁹ Therefore, PME is a slight negative than PZC. The knowledge of the PME is also useful to assess the stiffness of the interfacial water layer. For example, this has been revealed to be the main reason of energy barriers affecting charge and mass transfer through the interface.¹⁰

1.3 Laser-Induced Current Transient Technique

The illumination of a metallic electrode surface with intense laser light pulses can suddenly increase the temperature of the interfacial region. This method, which utilizes the so-called temperature jump effect is of increasing importance for electroanalysis in elucidating activated surfaces towards electron transfer, and the interfacial structure. For example, Benderskii et al. have reported studies on EDL (mainly the entropy of its formation) between a mercury electrode and an aqueous solution. Feldberg et al. also used this method to investigate kinetics of electrochemical processes. The sign of double layer charge was identified, then to obtain the location of PZC. Recently, Climent et al. have applied this method, but with a lower power of light to extract thermodynamic information about the double layer of Au (111)¹¹, and Pt (111)¹² electrodes.

The energy of beam and the wavelength of light are two key factors for this technique. For this lab course, light with a wavelength of 532 nm and beam energy with 200 mJ are used to probe the electrode/solution interface. However, the output of the beam energy is so high that it could damage most of working electrode. In this case, an attenuator is used to reduce and control the energy of beam towards the electrode.

About the temperature coefficient of the open circuit potential used for the dependence of Laser-Induced Current Transient Technique, one can show it from the electrocapillary equation like that:

$$\left(\frac{\partial E}{\partial T}\right)_q = - \left(\frac{\partial \Delta S}{\partial q}\right)_T$$

where ΔS represents the interfacial entropy of formation of the interface. One can obtain a plot of ΔS with integrating of a plot of the ΔE vs $\frac{1}{\sqrt{t}}$ as a function of the double layer charge. The curve ΔS vs q will reach its maximum, when the term $\left(\frac{\partial \Delta S}{\partial q}\right)_T$ is zero. That means the potentials of no current response are associated with the PMEs.

The orientation of the interfacial water molecules can change from “oxygen-up” to “oxygen-down” with the potential change. Noticeably, the orientation of the solvent molecules is

governed by the interactions between the molecules' dipole moment and the electric field generated by the electrode surface charge (E_{charge}). Owing to the large dipole moment, the potential drop of the electrode comes from the water molecules (E_{dipole}). The potential between the electrode and the solution ($E_{\text{M-S}}$) can be shown as:

$$E_{\text{M-S}} = E_{\text{charge}} + E_{\text{dipole}}$$

The rapid temperature jump could cause a disorder into the water layer for a quite short period of time. This can change the value of E_{dipole} and then the $E_{\text{M-S}}$ according to equation above. As a result, the charge of the electrode surface can be illustrated. In this case, two techniques of electrochemical analysis can be used. One is laser-induced potential transients (LIPT) in the coulostatic and another one is the laser-induced current transient (LICT) in potentiostatic mode, respectively. In this lab course, the latter one is utilized to record the current transients. The sign of the obtained transients corresponds to the sign of the electrode surface charge (**Figure 1.3**).¹²

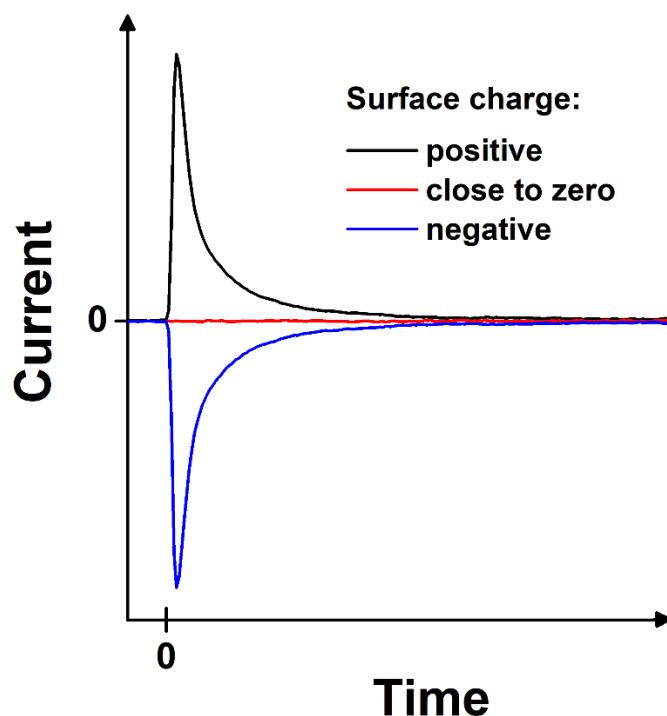


Figure 1.3. Orientation of the LICTs according to the excess surface charge of the electrode.

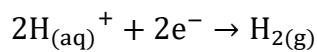
The sign of the current transient is strictly related to the sign of the surface charge.

Because of their ability to reveal the electrode surface charge, LICT technique is an easy tool to determine the PME and, related to it, the PZC. They can also serve in the evaluation of a mechanism and kinetics of various complex surface processes. Furthermore, one can also combine this technique with other commonly used methods (i.e., voltammetry, impedance spectroscopy) to make this technique particularly useful in a detailed characterization of various electrochemical systems.

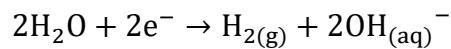
1.4 Hydrogen Evolution Reaction

Hydrogen gas is produced from the cathodic half-reaction of water splitting. This process named as the hydrogen evolution reaction (HER), is of great importance to a number of energy conversion devices, such as artificial photosynthetic cells or WELs. Depending on the pH level of the electrolyte used, the HER proceeds through the following reactions: Fehler! Textmarke nicht definiert.

In acidic media:



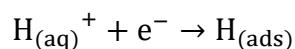
In alkaline solutions:



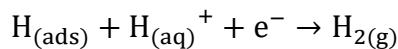
The thermodynamic equilibrium potential for the HER is given as $E^{\circ}_{\text{H}^+/\text{H}_2} = 0.00 \text{ V}$ vs reversible hydrogen electrode (RHE).

The reaction pathway can influence the kinetics of the HER (**Figure 1.4**). There are several steps in acidic media:¹³

- Volmer reaction (known as the discharged reaction) - is the process which is considered to be the fastest one. The electron transfer takes place at the catalyst surface in this process. As a result, an intermediate hydrogen atom gets adsorbed:



- Heyrovsky reaction (known as electrochemical desorption) - happens after the Volmer reaction. In this step a proton reacts with the adsorbed hydrogen under another electron transfer to form molecular hydrogen:



- Tafel reaction (known as the recombination reaction) - is a different process compared to the Heyrovsky reaction. In this case, molecular hydrogen is formed by two adsorbed hydrogen atoms:

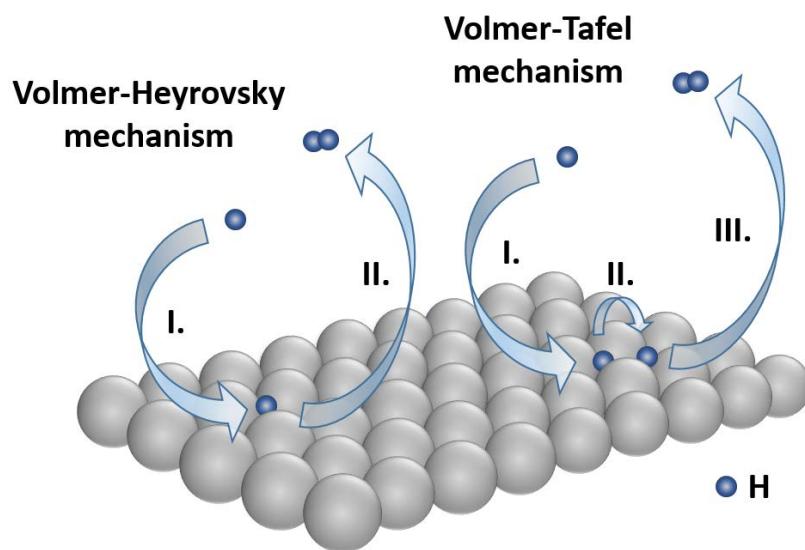
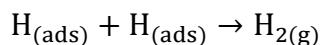


Figure 1.4. HER mechanisms on the electrode surface in acidic media. Roman numerals show the order of the subsequent steps.

As mentioned above, electrode materials, electrode surface structure and electrolyte composition can influence the HER kinetics. In this lab course, different pHs of $HClO_4$ solutions will be used to study the activity towards the HER to correlate it with the PME.

2. Experimental set-up

2.1 Electrochemical Cell

LICT measurements will be performed in a custom-built electrochemical glass cell using a three-electrode configuration (**Figure 2.1**). The cell has two main parts: (1) the preconditioning compartment and (2) the working compartment. One can purge the solution with gases in the preconditioning part and then introduce electrolyte into the working compartment where actual measurements are performed. This works for saving time and also, for example, getting rid of oxygen in the solution with purging Ar. A flat glass window located on second part was designed for laser transmission. For LICT measurement, one should put a working electrode (WE) towards glass window to make sure that laser beam can reach the electrode surface as much as possible.

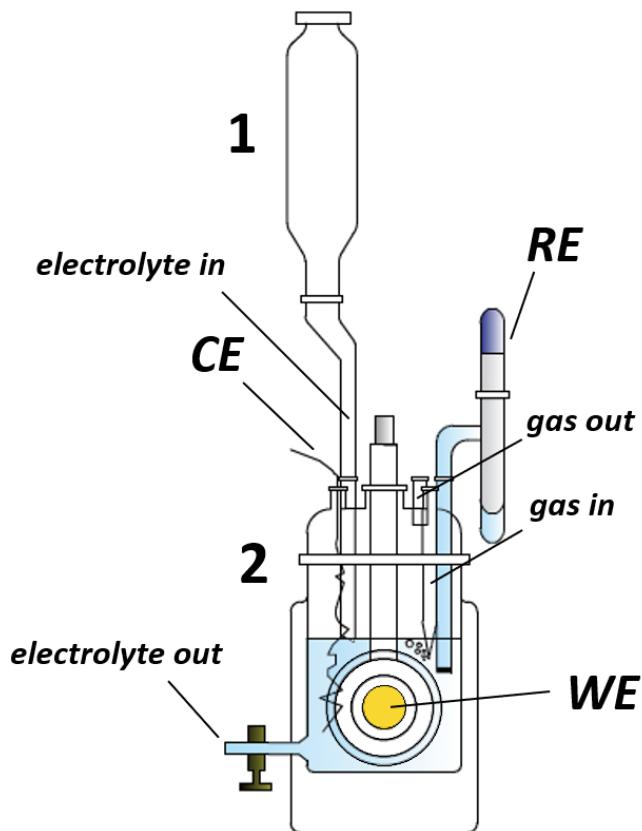


Figure 2.1. Scheme of the cell used for the LICT measurements. 1- preconditioning compartment; 2- working compartment. WE-working electrode, CE-counter electrode, RE-reference electrode

2.2 Setup for Laser – Induced Current Transient Technique

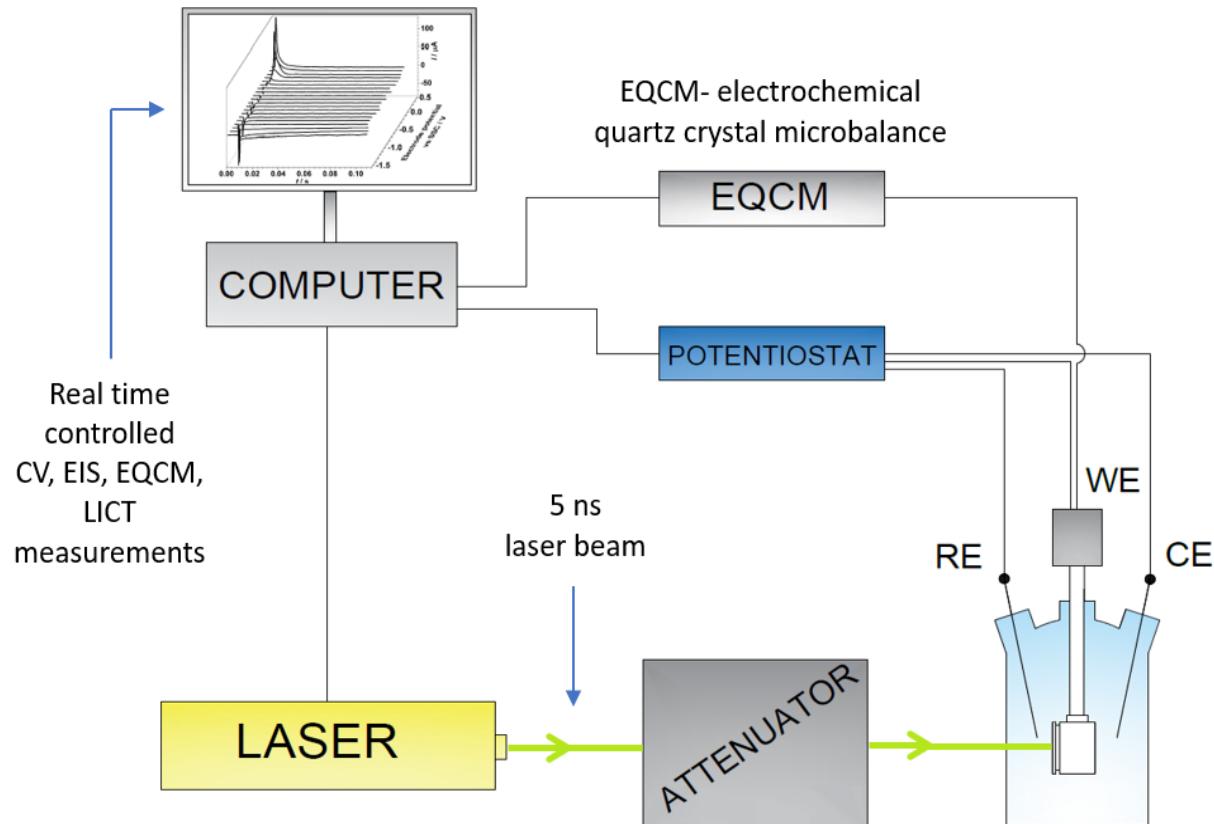


Figure 2.2. The Schematic illustration of setup for LICT measurements.

The LICT measurements in this lab course will be performed with a Quanta-Ray INDI-Series pulsed Nd:YAG laser. The repetition rate of the device is 10 Hz, while its pulse width and wavelength are 5-8 ns and 532 nm, respectively. This laser beam wavelength value is commonly used in studies employing laser-induced transient techniques. The choice of this value is typically motivated by the desire to avoid side effects, such as photoemission of electrons, as for numerous materials the photoemission threshold oscillates between 200 and 300 nm. The laser beam diameter is equal to ~9 mm. Along with the distance between the laser output and the WE the beam diameter will be kept constant. The energy of the laser beam directly at its output is ~200 mJ, which can result in the energy density of more than 300 mJ cm^{-2} . This value

is far above the damage threshold of most of the electrode materials. In order to reduce it, the beam will be passed through the attenuator. Transients are acquired by recording current alterations over time right after illuminating the electrode surface.

3. Experiments

3.1 Preparation of HClO₄ solutions

For this lab course, you need prepare three different pHs (pH = 0, 1, 2) of HClO₄ with 70% HClO₄ solution. Please calculate it before the experiment session and describe how to prepare it in your report.

3.2 Preparation of Electrode

For the preparation of the electrode surface crystal structure, the single crystals were flame-annealed with an isobutene gas flame and then cooled down in the mixture of CO (4.7, Air Liquide, Germany) and Ar (5.0, Air Liquide, Germany). The electrode surface structure quality was investigated by taking CVs in Ar saturated 0.1 M HClO₄ solution.

3.3 LICT measurements

In this lab course, the electrode/electrolyte interface will be probed with laser beam to reveal the electrode surface charge. The measurements will be conducted with the voltage ranges from 0.05 – 1.0 V vs RHE and the scan direction from higher potential to lower ones. All the LICT experiments are to be conducted using 20 mV potential steps.

4. Report

The report for this experiment should contain:

- 1) Short introduction of theoretical background.
- 2) A brief description of the performed experiments.
- 3) Explanation of the obtained measurements.
- 4) A brief conclusion for your measurements.

Additional questions for your report:

1. Why is three-electrode configuration used in this set-up?
2. Calculate and describe how to prepare these three different pHs ($\text{pH} = 0, 1, 2$) of HClO_4 with 70% HClO_4 solution.
3. Analyze your obtained data and find where PMEs locate for different electrolytes.
4. What is the tendency of HER activity with pH increase? Explain it with obtained PMEs results.
5. Can one extend the range of potential to more negative? Why?

5. References

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6. Safety Instructions

The Quanta-Ray INDI-Series Pulsed Nd:YAG Laser are Class IV-High Power Lasers whose beams are, by definition, safety and fire hazards. Both direct and reflected beams can cause severe eye or skin damage. Therefore, please observe the following precautions:

- a) Wear protective eyewear at all time.
- b) Avoid looking at the output beam; even diffuse reflections are hazardous.
- c) Avoid blocking the output beam or its reflections with any part of your body.
- d) Avoid wearing reflective jewelry while using the laser.
- e) Avoid passing through Laser Safety Curtains while using the laser.
- f) In case the laser is not operating, do not try to find the defect by yourself, but ask the tutor.

g) Do not change the power of laser without the instruction of the tutor.

Read these instructions carefully and ask the tutor if details are not clear.

I declare that I have taken note from the instructions above.

Date	Matriculation number	Signature