

**University of Ulm
Institute for Micro- and Nanomaterials**

**Lab
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B: Measuring the partial pressure by λ -sensor and ionic
conductivity in yttrium-stabilized zirconium-oxide
lab on July, 5th 2007

1 Questions

1.1 Questions to chapter 1.1 “Defects in Ionic Crystals“

Which atomic defects can appear in crystals?

In crystals following defects can appear:

- interstitial atoms: that means atoms which are on interstitial places in the lattice
- vacancies: that means places where an atom is expected are empty
- anti-structure atom: e.g. an anion is placed where a cation is expected
- impurity: another (foreign) atom is placed in the crystal
- double-vacancies: two atoms are missing, this can be two cations or two anions or an anion and a cation
- impurity-vacancy-complex: a foreign atom has been placed in the lattice which has forced the building of an vacancy due to the claimed electrical neutrality

Why will there always be defects in solids?

First, according to the equation $C_{vc} = e^{-G_s/2kT}$, in reality, the T has always some value, which leads C_{vc} to have a value, no matter how much it is. It means that in reality, there always exists vacancy defects with some concentration.

Second, in reality, the solid is nearly impossible to be a pure crystal, which means the solid always has some impurities, no matter how many they are.

Explain the Kröger Vink notation!

The Kröger-Vink Notation is set of conventions used to describe electrical charge and lattice position for defects in crystals. The general format is like M_S^C . The M stands for the defect, including atoms, vacancies, interstitial atoms, electrons and holes. S indicates the lattice site that the defect occupies and C corresponds to the electric charge of the defect relative to the site that it occupies. E.g. V_{Cl}^\bullet means a chlorine vacancy with singular positive charge and Ni_{Cu}^x means a nickel ion sitting on a copper lattice with neutral charge.

Are there differences between the creation of defects in ionic crystals and metals?

Ionic crystals have a crystal lattice with a regular alignment of ions. So the point defects can be caused by either anions or cations. But in metal, only metal cations have a regular alignment with electrons moving freely, which means the point defects can be only caused by metal cations. And, furthermore, the electric neutrality has to be kept in ionic crystals!

How can vacancies arise in ionic crystals? Which principles have to be considered?

Vacancies in crystals can arise due to the following mechanisms:

- **Schottky-Defect:** Anions diffuse out of the crystal and leave a vacancy and cause the creation of cation vacancies, because the principle of electrical neutrality cannot be violated.
- **Frenkel- and Anti-Frenkel-Defect:** This defect is restricted to one sublattice. Pairs of interstitial atoms and vacancies are built. If a vacancy on the cation-sublattice is built one speaks of Frenkeldefect, if a vacancy on the anion-sublattice is built, it's the Anti-Frenkel-Defect.
- **Dotation** Doping a material with impurities of different valency causes vacancies, too, because the electrical neutrality has to be kept.

How does the creation of vacancies occur in ZrO_2 and in Ca or Y stabilized ZrO_2 ?

In ZrO_2 the vacancies are created by the Schottky- or Frenkel/Anti-Frenkel-Defect. In stabilized ZrO_2 (which is doped by Ca or Y) the vacancies are built to keep the electrical neutrality.

So, for CaO, when introducing 1 mol Ca^{++} into the crystal, one mol of oxygen vacancies has to be formed. For Y_2O_3 , when introducing 1 mol Yttrium ions into the crystal, 0.5 mol of oxygen vacancies has to be formed.

1.2 Questions to chapter 1.2 “Diffusion and ionic Conduction“

How do the basic equations of diffusion look like and how can they be understood on atomic scale in a simple model?

There are two diffusion descriptions called Ficks first and second law. The first law is given by:

$$j_A = -D_A \frac{\partial c_A}{\partial x}$$

where j_A is the material flow, D_A is a measure for the mobility and c_A is the concentration of defects. So the law says, that the material flow j_A is given by the distribution of the concentration c_A of defects over the place x multiplied by a constant D_A which gives the mobility of the species.

The second law is given by:

$$\frac{\partial c_A}{\partial t} = \frac{\partial}{\partial x} \left(D_A \frac{\partial c_A}{\partial x} \right)$$

This law expresses the time derivity of the diffusion.

What connection consists between the micro- and macroscopic description of diffusion?

The macro- and microscopic description of diffusion is given by the **Einstein-Smoluchowski-Equation** $D = \gamma a^2 \Gamma$, where D is the diffusion coefficient, γ is factor (in diffusion matters it is 2, a^2 is the place and Γ is the hopping rate.

What kind of diffusion mechanism do exist? Explain their principle!

There are mainly two diffusion mechanisms:

- **Vacancy Mechanism:** A cation or anion moves to a neighboured vacancy.
- **Interstitial Mechanism:** a anion moves between cations on a interstitial place.

How can the temperature dependence of the diffusion coefficient be derived for the different mechanisms?

The temperature dependence of the diffusion coefficient is given by the Arrhenius Law as

$$D \propto \exp\left(\frac{-E_{akt}}{kT}\right)$$

for the vacancy mechanism with $E_{akt} = E_V^m + E_V^f$ being the activation energy and as

$$D \propto \exp\left(\frac{-E_i^m}{kT}\right)$$

for the interstitial mechanism, whereby E_i^m is the migration energy.

What has to be taken into account for a high structural concentration of vacancies?

For a high structural concentration of vacancies it can be assumed that in the vacancy mechanism the number of extrinsic vacancies is much bigger than the number of intrinsic vacancies, so $E_{akt} = E_V^m$ with E_V^m being the migration energy of vacancies.

How is the ionic conduction in ionic crystals connected with diffusion? Which temperature dependence of the ionic conduction results from this?

The connection between ionic crystals and conduction is given by the Nernst-Einst-Einstein

$$\frac{D}{kT} = \frac{\sigma}{cq^2}$$

with D being the diffusion coefficient, T being the temperature, σ the conductivity and q the charge.

1.3 Questions to chapter 1.3 “Solid Oxygen-ion Conductors“

What is a solid oxygen-ion conductor and which requirements does it have to fulfill?

A solid oxygen-ion conductor is a conductor where the conduction and so the current is based on ion transport.

Explain the crystal structure of pure ZrO_2 !

The structure of pure ZrO_2 is depending on temperature: it can be monoclinic, cubic or tetragonal.

Which phases are passed for example during cooling from 2500 °C and what problem results from this for applications of the ceramics?

At 2500 °C ZrO_2 is cubic, then it is tetragonal until ca. 1200 °. Under 1200 ° the structure is monoclinic. Due to these phase transitions a jump in the volume occurs, which can destroy the ceramics.

How can this problem be solved?

By doping the ZrO_2 with CaO the cubic phase is stabilized down to room temperature and so a destruction is prevented.

What other often desired effect appears then?

Due to the doping with atoms of other valency vacancies have to be built to keep the electrical neutrality. The resulting high vacancy concentration leads to a higher mobility of the oxygen ions and so to a higher conductivity.

Can the ionic conductivity of ZrO_2 be continuously increased by higher and higher doping concentrations? (reason!)

In the doping process the host matrix is not changed. We want to operate in the cubic phase, so a doping of 4-8% is sufficient.

How does the electronic conductivity behave in ionic crystals?

Typically those structures are bad electron conductors as the electrons are trapped very easily by positive charges in ionic crystals. The electronic conductivity is several decades smaller than the ionic conductivity.

How does the setup of a galvanic cell typically look like for which a solid electrolyte of stabilized ZrO_2 is used?

Two platinum electrodes are attached to the oxygen-ion conductor and exposed to different oxygen partial pressure.

Explain the functioning of the cell! How can the cell voltage be calculated?

With the above mentioned arrangement a galvanic cell is formed which is called “solid electrolyte“. At the platinum layer the necessary oxidation and reduction processes take place. If there are enough oxygen vacancies in the solid electrolyte, the oxygen ions are integrated in the so called three-phase-boundary and diffuse along the diffusion gradient to the other electrode. By leaving the electrolyte the ions release two electrons. So a potential difference which can be measured, is build up. The cell voltage U_{12} can be calculated by the Nernst Equation as

$$U_{12} = \frac{kT}{4e_0} \ln \left(\frac{p_2}{p_1} \right)$$

where p_1 and p_2 are the two different pressures and e_0 the charge of the released electrons.

How can derivations of the ideal behaviour of the cell emerge?

Derivations may occur due to two effects: One is the conductivity of the electrolyte, which is decided by the real motion of oxygen ions in the crystal, not just decided by P_1 and P_2 . The other is that when with a high current, it is limited by the reactions at the electrodes, which is not reflected in the equation $U_{12} = kT/4e_0 \ln(P_1/P_2)$

1.4 Questions to chapter 1.4 “Application of stabilized ZrO_2 in the motor vehicle technology“

Explain in short the formation of flue gas in a gasoline engine!

Flue gas may include oxygen (air), e.g. CO, HC, CO_2 , NO_x , H_2O , SO_2 and so on.

How is the air number λ defined and what is its meaning?

The air number λ is defined as

$$\lambda = \frac{m_{air}^{real}}{m_{air}^{theo}}$$

It is the proportion of really mass of air offered to burn 1 kg of fuel to the theoretical amss of air you need to burn the fuel completely.

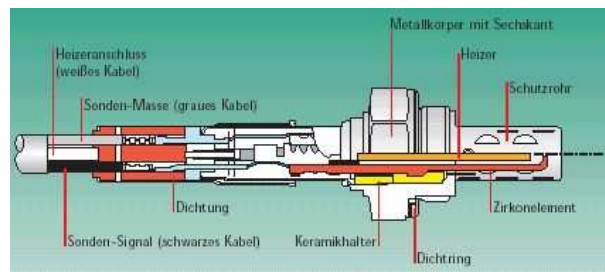
How are pollutants generated in the flue gas and what impact do they have on the environment?

Pollutants are generated if too much oder too less air is offered for the burning process. In the first case oxygen is left, in the latter case carbon monoxide is built and hydrocarbons remain.

Carbon monoxide is one of the reasons for global heating and the ozone hole.

Describe the configuration of the λ -sensor and the function of the individual parts!

As active sensor ceramics a solid electrolyte of Y_2O_3 doped ZrO_2 is used like described in the previous chapter. The sensor voltage also results from the Nernst Equation. To reach operation temperature as soon as possible an active sensor heating is used. In addition the active ceramics is secured by further protective measures like a metallic protective pipe and another ceramic coating to avoid early destruction by erosion due to the high flow velocities and the temperature shocks. The main part of the λ -sensor has: sensor frame, ceramic buttress pipe, connecting cable, protective pipe with slits, active sensor ceramics, contact part, protective ring, heat element clamps for the heating element.



How does the characteristic line of the λ -sensor arise?

The characteristic line of a λ -sensor arises at the value of $\lambda=1$ by approximately 800 mV due to the catalytic effect of platinum. This jump in voltage can easily be used as a control signal.

What's the function of the λ -sensor for cleaning the flue gas?

The λ -sensor can give a precise signal to keep $\lambda = 1$. For example, when $\lambda < 1$, which means an oxygen excess, it will control to let more fuel in. When $\lambda > 1$, which means an oxygen lack, it will control to let less fuel in. In short, it keeps the combustion work "ideal", which in some degree means cleaning the fuel gas.

Explain the terms "controlled catalyst" and "three-way catalytic converter"!

A controlled catalyst is a combination of a λ -sensor and of a three-way-catalytic converter. A three-way-catalytic converter means a catalytic converter, where all three pollutants CO, HC and NO_x are decomposed simultaneously.

2 Carrying Out The Experiment

2.1 Principle

2.1.1 Lambda Sensor

The lambda sensor is a potentiometric oxygen sensor on zirconiumoxide basis. It is applied in motor vehicles with a gasoline engine to measure the oxygen partial pressure in the waste gas and draw conclusion on the combustion. As active sensor ceramics a solid electrolyte of Y₂O₃ doped ZrO₂ is used because of the following reasons.

1. It stabilizes the cubic phase of the fluoride structure of ZrO₂ down to room temperature and inhibits the mechanical destruction.
2. The yttrium ions are built in on zirconium sites. Due to the aliovalence of the yttrium ions (Y³⁺) compared to the zirconium ions (Zr⁴⁺) vacancies are created to keep up the electric neutrality of the crystal. Therefore $\frac{1}{2}$ mole of oxygen vacancies has to be formed when integrating 1 mole of yttrium ions into the crystal. This high vacancy concentration on the oxygen sublattice increases the mobility of the oxygen ions tremendously and is reflected in a strong increase of the oxygen ion conductivity.

The sensor voltage also results from the Nernst equation:

$$U = \frac{kT}{4e_0} \ln \frac{p_{\text{O}_2}^{\text{air}}}{p_{\text{O}_2}^{\text{gas}}}$$

To reach operation temperature as soon as possible an active sensor heating is used. In addition the active ceramics is secured by further protective measures like a metallic protective pipe and another ceramic coating to avoid early destruction by erosion due to the high flow velocities and the temperature shocks.

2.1.2 The Air Number λ

The air number is a measurand of combustion technology and is defined in the following way

$$\lambda = \frac{m_{\text{air}}^{\text{real}}}{m_{\text{air}}^{\text{theo}}}$$

Here $m_{\text{air}}^{\text{theo}}$ means the theoretical mass of air to burn 1 kg of fuel and $m_{\text{air}}^{\text{real}}$ indicates the actually offered mass of air during the combustion process.

The meaning of λ is

- $\lambda = 1$: As much air for the combustion is offered as theoretically necessary. The combustion works "ideal".
- $\lambda > 1$: More air is offered as theoretically necessary. This is called *meager mixture*, in the flue gas there is an oxygen excess
- $\lambda < 1$: Too less air is used for the combustion. The mixture is called "fat", in the flue gas there is unconsumed fuel

The two latter cases have negative effects on the appearance of pollutants. With $\lambda > 1$ nitrogen oxides are created and with $\lambda < 1$ too less oxygen is available - carbon monoxide and unburnt hydrocarbons remain.

Annotation: Though the pollutant concentration in a real combustion process is minimal with $\lambda = 1$, it is still remarkable. Even at $\lambda < 1$ there still is a certain amount of pollutant concentration left. This is caused by the fact that the combustion is not ideal as it has to proceed in finite time and the building of the mixture is not homogenous.

2.1.3 The function of the λ -sensor

The λ -sensor has its name from the characteristic of reacting very sensitively on deviations from $\lambda = 1$, i.e. on deviations from the stoichiometric composition of a mixture. Figure 1 above shows a typical characteristic curve of a λ -sensor. Within a small range around $\lambda = 1$ the sensor voltage jumps by approx. 800mV, which can be used as a precise controlling signal.

The reason for it is the catalytic effect of the platinum coating. This assists further oxidation of the not completely burnt hydrocarbons to H_2O and CO_2 and of CO to CO_2 with the remaining oxygen in the flue gas. So for $\lambda = 1$ locally at the inner electrode a depletion of oxygen takes place and so leads to a steep increase of the sensor voltage. The sensor measures the equilibrium oxygen partial pressure of the flue gas. No adjustment of the equilibrium takes place at the electrode and so the signal of the sensor is only determined by the rest oxygen content.

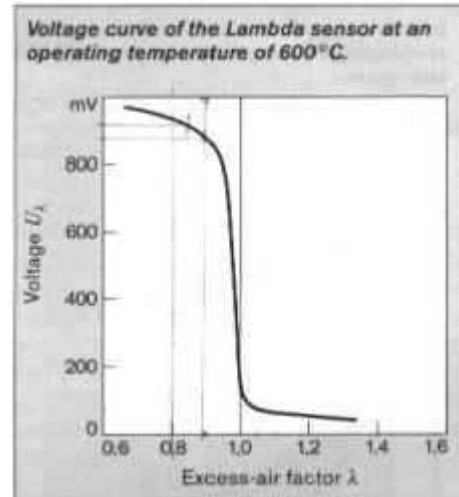


Fig. 1: sensor voltage over air number λ

2.1.4 Flue Gas Cleaning for Gasoline Engines

The catalytic effect of the λ -sensor doesn't suffice of course to clean the flue gas. Modern systems use a "controlled catalytic converter", a combination of λ -sensor and three-way catalytic converter. The label "three-way" refers to the fact that all three pollutants CO , HC and NO_x are simultaneously decomposed. This catalytic converter consists primarily of a ceramic netting with big surface, that is coated with platinum and rhodium and assists the chemical decomposition of the flue gases. Thus the effect of the catalyzer is only optimal for stoichiometric composition of the flue gas. Technically this is not only achieved by calculation the composition of the mixture, but by a so called closed controlling circuit which controls the result of the combustion. Therefore the λ -sensor is responsible.

2.2 Nernst Equation

The first task of the experiment was to measure the voltage of the sensor when it was exposed to oxygen partial pressure.

This task was to prove the relation in Nernst equation.

Two values of heating voltage (11.5 V and 12.5 V) were studied to see the effect of temperature change. The sensor was exposed to different values of oxygen flow rate from 3.30 down to 0.00 with a 0.05 interval for 11.5 V heating voltage and a 0.10 interval for 12.5 V.

The temperature of the gas chamber remained the same at 276 °C at both measurements; whereas, that of the sensor increased from 491 °C to 492 °C due to the increase in heating voltage.

Below the results of this experiment are plotted (fig. 2)

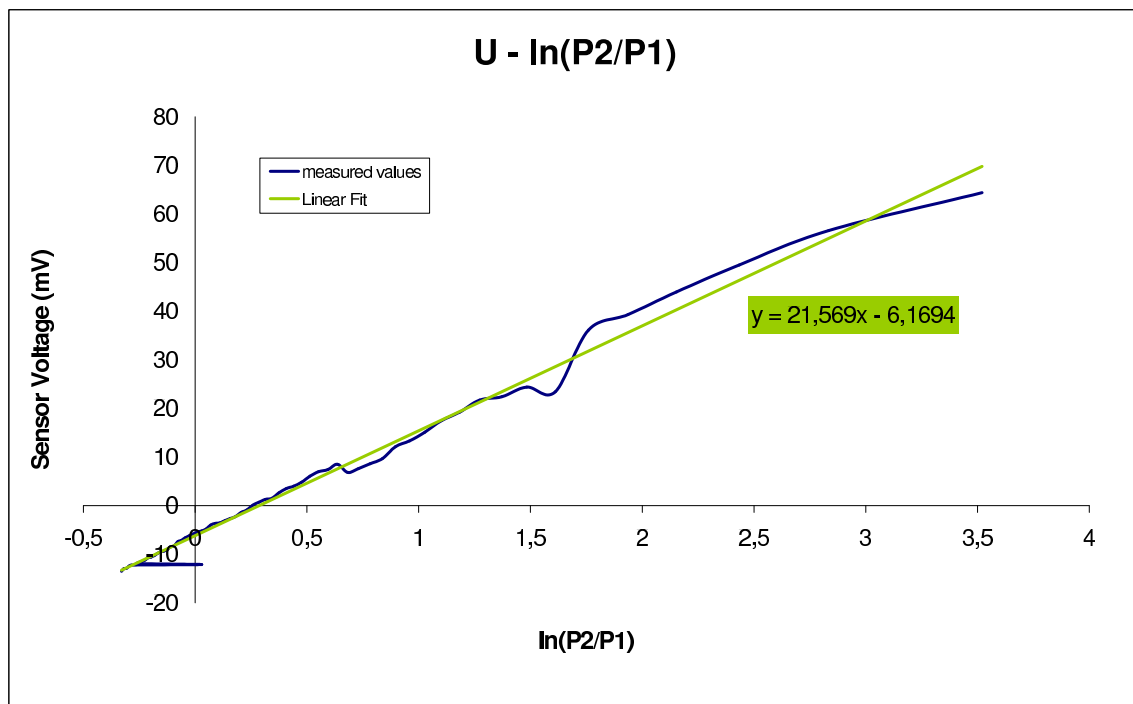


Fig. 2: $U - \ln \frac{p_{O_2}^{air}}{p_{O_2}^{gas}}$ at a heating voltage of 11.5V

From the Nernst Equation $U = \frac{kT}{4e_0} \ln \frac{p_{O_2}^{air}}{p_{O_2}^{gas}}$ follows, that in the case that if both pressures are equal, the voltage should be zero. In our measurement the voltage at this point isn't equal to zero but it is $U(p_{O_2}^{air} = p_{O_2}^{gas}) = -6.1694mV$. This value indicated that there still remained oxygen in the chamber. To calculate the remaining oxygen we used the sensor

voltage measured when only nitrogen was left in the chamber ($U_{\text{onlynitrogen}} = 107.47$). So we got for the remaining oxygen a value of:

$$\frac{0.28}{e^{107.47 \cdot 10^{-3} \cdot 4 \cdot 1.6022 \cdot 10^{-19} / 1.38 \cdot 10^{-23} \cdot 764.15}} = 4.0795 \cdot 10^{-5}$$

Now we performed the same measurement at a higher heating voltage (12.5 V). Plotting the measured result gives us the following graphics (fig. 2):

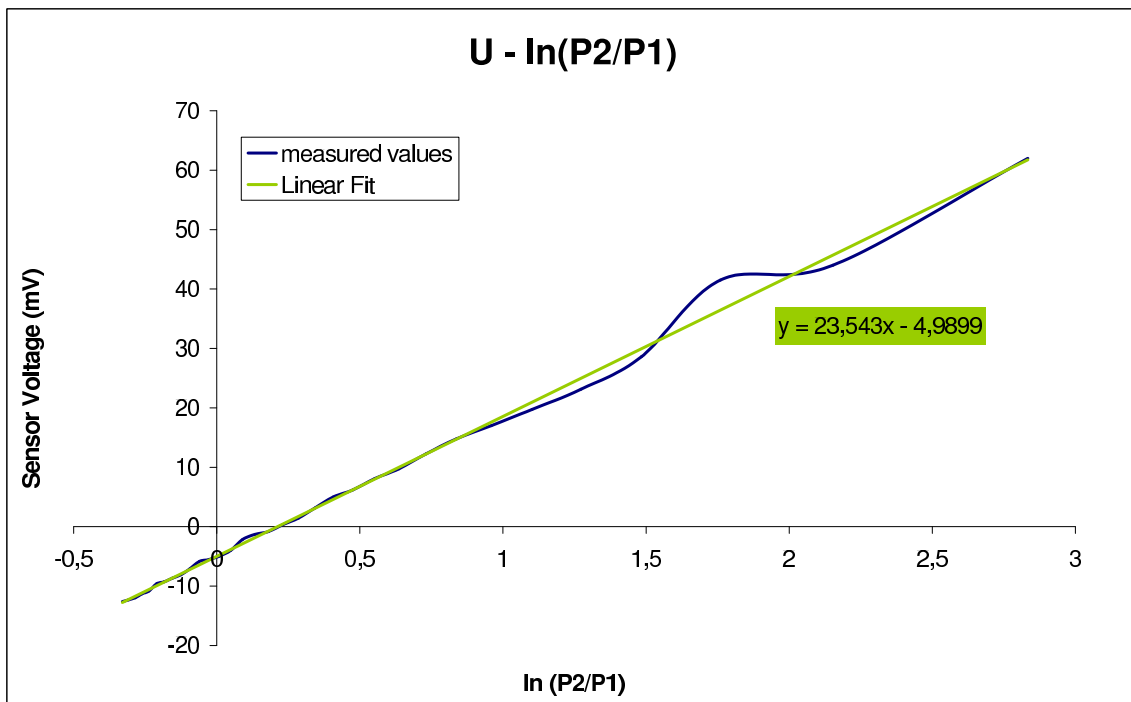


Fig. 3: $U - \ln \frac{P_{O_2}^{air}}{P_{O_2}^{gas}}$ at a heating voltage of 12.5V

At a higher heating voltage, the relationship between sensor voltage and $\ln \frac{P_2}{P_1}$ was found to be similar to the one at a lower heating voltage. The difference was that the values for the sensor voltage was significantly higher due to more heat contributed to the equation. At the oxygen flow rate of 2.13 where it should exhibit the zero voltage, in the experiment the sensor voltage was found to be around 4.9899 mV; hence, the remaining oxygen was approximated to (using the value of 112.60 mV when only nitrogen was left into the chamber).

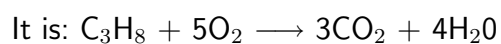
Here we got an remaining oxygen of:

$$\frac{0.22}{e^{112.6 \cdot 10^{-3} \cdot 4 \cdot 1.6022 \cdot 10^{-19} / 1.38 \cdot 10^{-23} \cdot 765.15}} = 2.390 \cdot 10^{-4}$$

From the slope of the measured curves we can check if the Nernst Equation is fulfilled, as the slope stands for the factor $\frac{kT}{4e_0}$. Calculating the expected value of the slope we get a value of 16.4543 for the 491°C-probe and a value of 16.4758 for the 491°C-sample. The measured values are 21.569 and 23.543. That means that we have an error of 24% and 31%. This quite big errors may be due to the fact that our curves are not really linear, what may be due to the measurement.

2.3 Catalytic Effect

The second task of the experiment was to look at the catalytic effect of the lambda probe when the value of lambda was close to 1. Propane was used as a source for combustion.



The following table shows the values of lambda against their corresponding sensor voltage.

Propane (l/min)	Oxygen (l/min)	U (V)	λ
0.025	0.03	1.1	0.24
0.020	0.03	0.9	0.3
0.015	0.03	0.83	0.4
0.010	0.03	0.78	0.6
0.005	0.03	0.10	1.2
0.0025	0.03	0.093	2.4

Plotting this values gives us the following graph (fig. 4)

For lambda equal to 1, the voltage was found to be 0.23 V.

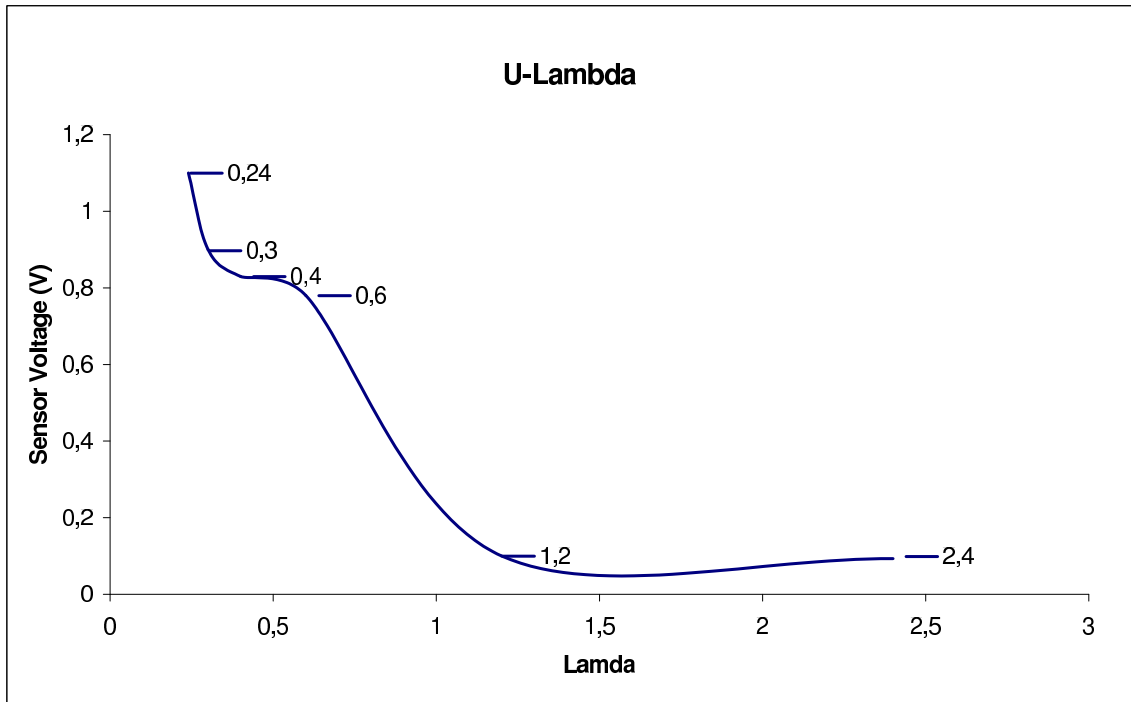


Fig. 4: Sensor Voltage over λ

2.4 Negative Temperature Dependent Voltage

The last task of the experiment was to observe the negative temperature-dependent voltage. It was proposed that when exposed to air (oxygen flow rate of 2.13 l/min against nitrogen flow rate of 8 l/min), the sensor showed a negative dependency on temperature.

We measured the sensor voltage when the sensor was heated using different values of heating voltage from 12.5 V down to 9.0 V with a 0.5 V interval.

Heat.Volt. (V)	Sensor Volt. (mV)	Temp. λ -probe (°C)	Temp. chamber (°C)
12.5	-4.00	48.8	28.5
12.0	-1.88	48.5	28.6
11.5	-2.14	48.5	28.6
11.0	-2.30	48.4	28.5
10.5	-3.49	48.4	28.3
10.0	-4.47	48.3	28.2
9.5	-5.71	48.3	28.1
9.0	-9.40	48.3	28.9

From the data in the Table.2 there seemed to be a gradual decline of the sensor voltage when

the heating voltage was reduced step by step with an exception of the first measurement when the temperature was the highest. This however disagreed with the proposition which stated that the relationship between the voltage and the temperature should be reversal.

In the figures 5 and 6 you can see the increase of the sensor voltage in dependence of the heating voltage (which is \ln -shaped) and the gas chamber temperature in dependence of the sensor voltage (which is e -shaped).

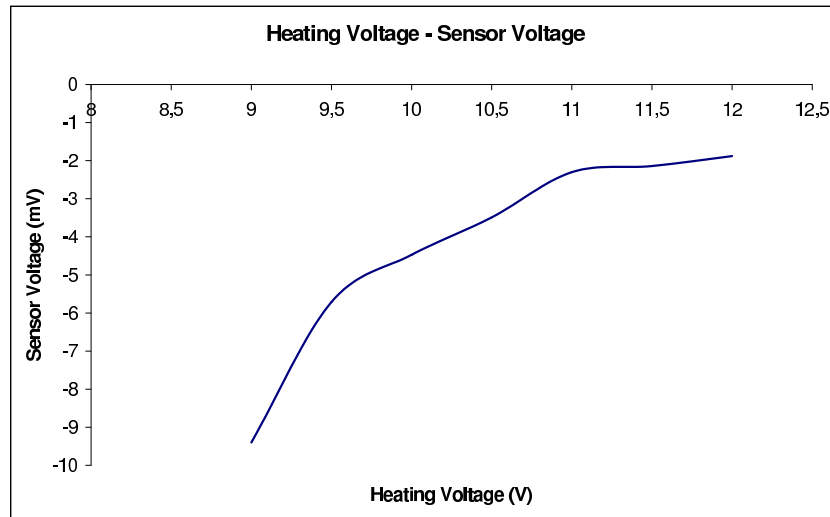


Fig. 5: Sensor voltage in dependence of heating voltage

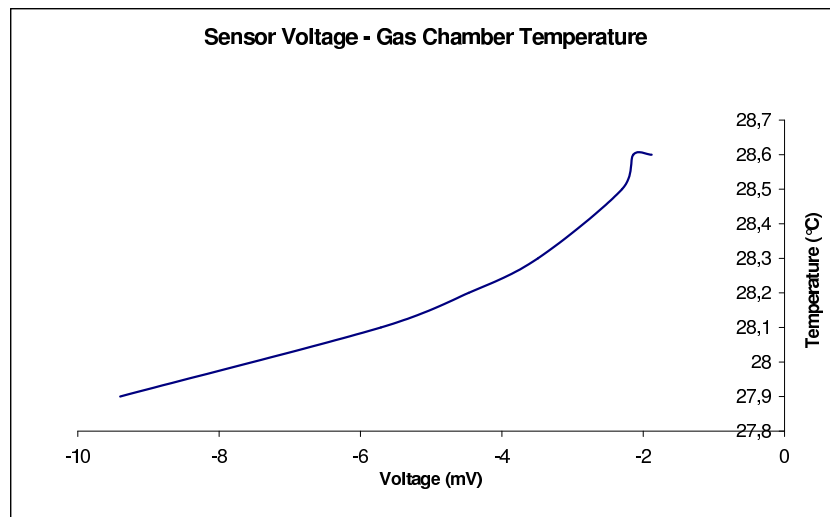


Fig. 6: Gas chamber temperature in dependence of the sensor voltage