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**KINETIC STUDIES OF THE RESPONSE TIMES OF
ZIRCONIA OXYGEN SENSORS**

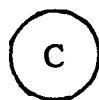
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Anita Sharma

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

at

Dalhousie University
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February, 1994



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Abstract

Two oxygen sensors, A and B, employing yttria-stabilized zirconia as an electrolyte and platinum paste as electrodes, were studied using three techniques, namely exposing the sensor to rapid changes in oxygen pressure, complex impedance measurements and scanning electron microscopy.

By exposing the sensor to rapid changes in pressure, response times were measured from 760 to 8 torr and at temperatures between 773 and 948 K for sensor A and between 623 and 823 K for sensor B. Experiments in which the oxygen pressure suddenly increased had faster response and the opposite dependence of response on initial pressure when compared to experiments in which the pressure suddenly decreased. For sensor A, the order of the response times with respect to final oxygen pressure was found to be about $-1/4$ at 773 K, decreasing at higher temperatures. For sensor B, the order of response with respect to the pressure was close to zero at all temperatures. The activation energy was found to be 210 ± 14 kJ mol⁻¹ for sensor A and 145 ± 14 kJ mol⁻¹ for sensor B. The logarithm of the pre-exponential factor in units of s⁻¹ was 12.4 ± 0.5 for sensor A and 9.7 ± 1.2 for sensor B. The differential rate equations for various possible elementary steps were integrated and the resulting expressions were fitted to experimental curves of voltage as a function of time. Scanning electron micrographs were used to measure the electrode/electrolyte contact area for sensor A. For sensor A, the results at lower temperatures were in agreement with a model in which response is limited by the rate of conversion of electron holes and singly-charged oxide anions to neutral oxygen atoms at the surface of the zirconia. At higher temperatures, the reaction of oxide anions with electron holes could be rate limiting.

Using the complex impedance technique for sensor B, the bulk and interfacial resistance and capacitance were determined at 623 to 823 K. The activation energy for the bulk conductance was 80 ± 17 kJ mol⁻¹ and for the interfacial conductance was 119 ± 17 kJ mol⁻¹. The results from the impedance experiments and response time measurements were consistent with a mechanism in which the rate is limited by diffusion of electron holes from the bulk to the electrode/electrolyte interface.

Abbreviations

C_i	Interfacial capacitance
C_b	Bulk capacitance
D_h	Diffusion coefficient of electron holes
ΔE	Change in voltage
E	EMF of the cell
E_a	Activation energy
F	Faraday's constant
f_{max}	Frequency at the top of the semicircle
h	Electron hole
α	Angle of depression
t_i	Ionic transference number
t_e	Electronic transference number
Z	Complex impedance
Z^*	Complex conjugate of Z
ϕ	Phase shift
R_s	Resistance in series with the sensor
R_i	Interfacial resistance
R_b	Resistance due to the bulk
ϕ_i	Chemiflux

r	reservoir
λ	molar conductivity
$t_{1/2}$	Time when the voltage reaches half its Nernstian value
$t_{0.63}$	Time when the voltage reaches 63 % of its Nernstian value

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INTRODUCTION

1.1 Stabilized Zirconia

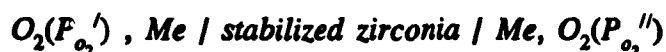
Stabilized zirconia is capable of conducting oxide ions over wide ranges of temperature and oxygen potential.¹ Because of this property, it is used as a solid electrolyte in various types of electrochemical cells in laboratories and industries. Kiukkola and Wagner² first reported the measurement of oxygen potential using stabilized zirconia as a solid electrolyte in an oxygen concentration cell. Zirconium is a tetravalent element and its oxide, ZrO_2 , crystallizes with a distorted fluorite structure.^{3,4} When zirconia is doped with a metal oxide with a cation of lower valency, it forms a solid solution and acquires a stable cubic fluorite structure and is called stabilized zirconia. Commonly used lower valent oxides are Y_2O_3 and CaO . The difference in the valencies of the two cations in the mixed oxide leads to a deficiency of oxide ions in the anionic part of the crystalline lattice. The extent of oxygen deficiency depends upon the amount of dopant oxide added.⁴ Introduction of two trivalent cations gives rise to one anion vacancy thus maintaining charge neutrality in the crystalline lattice. Oxygen ion conduction occurs via this defect structure. In stabilized zirconia, the anions are the predominating conducting species.⁵ In calcia-stabilized zirconia, anion diffusion is at least

six orders of magnitude faster than cation diffusion at 1273 K.^{1,3}

1.2. Zirconia Oxygen Sensors

1.2.1. Principle

A zirconia oxygen sensor is a type of concentration cell in which stabilized zirconia is used as an electrolyte (oxide ion conductor), noble metals like Pt, Au or Ag or conducting oxides based on solid solutions of UO_2 are used as electrodes and oxygen with different partial pressures is present in the two compartments. The cell can be represented as,



here P_{O_2}' and P_{O_2}'' are two different partial pressures of oxygen and Me is the electrode.⁶ One of the pressures of oxygen is the reference and the other is the unknown. Air is usually used as a reference as the partial pressure of oxygen is fairly constant in air.

The zirconia oxygen sensor is usually in the form of a tube made of the electrolyte and closed at one end. The tube can be a few cm to more than 50 cm long with a diameter from less than 1 cm to 2-2.5 cm. The size of the sensor depends upon its application. Depending upon the application, either side of the sensor can be used for the reference electrode. In the laboratory, the outside is usually used as the reference whereas the inside is used for the reference electrode for industrial applications.⁷

When the two opposite sides of the electrolyte are in contact with oxygen at

different partial pressures, the oxygen with the greater partial pressure has the tendency to acquire electrons and enter the electrolyte as oxide ions, occupying the vacant lattice sites, as represented by the following reaction,⁸



where $\text{V}_{\text{O}}^{\cdot\cdot}$ is a vacancy at a normal oxygen site in the crystalline lattice of the electrolyte, e^- is a electron taken from the electrode and $\text{O}_{\text{O}}^{\cdot\cdot}$ is a mobile oxide ion in the anionic lattice. Oxide ions in the anionic lattice have a tendency to lose electrons and form gaseous oxygen on the side of the electrolyte with the lower partial pressure of oxygen. This reaction can be written as,



As a result, a positive potential is developed on the side with the higher partial pressure of oxygen and a negative potential is developed on the opposite side. This potential, E , developed across the electrolyte, is related to the partial pressure of oxygen on the opposite sides and is given by,⁷⁻¹⁰

$$E = \frac{RT}{4F} \int_{P_{\text{O}_2}'}^{P_{\text{O}_2}''} t_i d \ln P_{\text{O}_2} \quad 1.1$$

here T is the absolute temperature, R is the gas constant, F is Faraday's constant and t_i is the ionic transport number. The sensor output voltage, E , is in the form of an electrical signal.

Under ideal conditions, the electrolyte is impermeable and the conduction through

¹ Throughout the thesis, square brackets will be used for numbering all the chemical reactions. All the mathematical equations will be numbered in decimal form.

the ceramic is totally ionic,⁵ i.e. $t_i = 1$. Then the expression simplifies to the well known Nernst equation,⁷⁻¹⁰

$$E = \frac{RT}{nF} \ln \frac{P_{O_2}'}{P_{O_2}''} \quad 1.2$$

Here it is assumed that the electrodes behave in a reversible manner and the electrolyte, electrode and gas on each side are in thermodynamic equilibrium. Since the values of R , F , T and $P_{O_2}(\text{ref})$ are known, the unknown P_{O_2} can be determined by measuring the EMF of the cell.

1.2.2. Applications of Sensors

Zirconia oxygen sensors are used in a variety of important processes.

1.2.2.1 In Automobiles

Sensors are used in automobiles to improve the efficiency and fuel economy of engines by reducing harmful exhaust emissions and consumption of fuels.¹¹⁻¹⁵ The sensor used is in the form of a thimble and the inner and outer surfaces are coated with porous platinum. The sensor is located in the exhaust manifold, the outer electrode is exposed to the exhaust emissions and the inner electrode is exposed to air, which is the reference gas. The temperature in the exhaust manifold ranges from 573-1173 K.^{15,16} The flow rate of the gases in the exhaust manifold also varies widely and could go up to 150 ms⁻¹.¹⁵

The partial pressure of oxygen in the exhaust gas depends on the air to fuel (A/F) ratio and the electromotive force (EMF) of a sensor shows an abrupt change at the stoichiometric point. The electrical signal obtained from the sensor indicates whether the exhaust gas is richer or leaner than the stoichiometric mixture. Response of the sensor to small changes in the A/F ratio is important for this application. There is an increasing interest in lowering the operating temperature of the sensor.

1.2.2.2 In Metallurgical Processes

In metallurgical applications, the sensors are used to determine the oxygen content of molten metals at high temperature.^{7,10} In the steelmaking process, it is necessary to control the concentration of oxygen for proper deoxidation, steel cleanliness, good yield and quality of the final product. The oxygen concentration is determined at various stages in the process where the temperature is about 1873 K. A sensor, in the form of a pellet fitted into a quartz or ceramic tube, is inserted into the liquid metal and the output voltage is recorded to its maximum, which corresponds to the oxygen content of the metal. The sensor is disposed of after a single use as the temperature is high and the sensor becomes corroded.⁷ For this application it is required that the change in sensor output voltage be fast with change in temperature.

Zirconia oxygen sensors could also be used for monitoring the concentration of silicon, sulphur, phosphorus and aluminum in molten iron.¹⁷

1.2.2.3 In Combustion Control

Zirconia oxygen sensors are used in combustion control of several types of furnaces, which include boilers, metallurgical and glass tank furnaces, in order to maintain a uniform and efficient combustion process.^{7,18} For maximum efficiency, 0.5 % excess air is required but in the absence of a controlling device, 25-50 % of excess air is used, resulting in poor fuel efficiency.⁷ The sensors are used for closed loop control of the A/F ratio. The important features to be considered for this application are the design of the sensor and its location in the furnace.⁷

1.2.2.4 For Measuring the Oxygen Pressure in Inert Gases

Sensors are used for measuring the oxygen pressure in inert gases or in vacuum in the range 10^{-6} - 1 atm.^{8,19,20} This corresponds to 0 - 300 mV variation in the sensor output voltage when the reference gas is air.¹⁹ The temperature in such devices is around 873-1073 K. Oxygen permeation through the ceramic limits its use at very low pressures.⁸

1.2.2.5 For Atmospheric Control in Heat Treatment Furnaces

Zirconia oxygen sensors are used for atmosphere control in heat treatment furnaces^{7,21} where it is necessary to maintain an accurate pressure of oxygen in order to achieve fuel economy and greater efficiency. Metals like stainless steel, copper, brass, nickel and aluminum are annealed under reducing conditions to avoid surface oxidation. It is

therefore necessary to maintain a suitable pressure of oxygen during the annealing. The sensor output is used for closed loop control of the A/F ratio to obtain the desired pressure of oxygen.⁷

1.2.3. Response time studies on sensors

The time of response of the sensor to rapid changes in pressure and/or temperature is an important factor in many of its applications, where it is used for feedback control. Response time depends on many factors, such as temperature, concentration range²², composition and morphology of the electrode²³⁻²⁵ and the nature of the electrolyte.^{24,25}

Only a few studies have been reported on the response times of zirconia oxygen sensors. Heyne and Engelsen²⁶ did theoretical studies on the factors which affect the speed of response of solid electrolyte gas sensors and suggested that the uptake or release of gas by the sensor is the main reason for sluggishness and for the change of sensor voltage with time. They predicted that when the pressure of oxygen is suddenly changed on one of the electrodes, the emf would not change instantly but would show some delay. They suggested that for a voltage change to occur, a finite amount of the gas has to be supplied or taken away from the system and this takes some time. So the emf changes slowly during this transition and becomes stationary after this time, which they considered to be the response time of the sensor.

Fouletier et al.²² determined the time lag (time required for the voltage to change by 99% of its total value) for Pt and Ag electrodes on yttria stabilized zirconia sensors.

The pressure of oxygen was changed by connecting two chambers containing gases of the same composition but at different pressures. They observed that the time lag depended upon whether the change was an increase or decrease of pressure. The time lag was longer when the pressure was changed from high to low than when the pressure changed from low to high. Using a constant ratio of the initial and final pressures, they studied the effect of oxygen pressure on the response time and found it to be inversely proportional to the square root of the average pressure.

Anderson and Graves²⁷ examined the transient voltage response for zirconia oxygen sensors for step changes in the gas composition. They also found that the voltage response was slower when the partial pressure of oxygen was changed from high to low than from low to high. They found that the corresponding curves of oxygen partial pressure, derived from experimental voltages using the Nernst equation, were symmetric as a function of time. They suggested that the asymmetry in the two types of voltage response curves was due to the logarithmic dependence of sensor voltage on partial pressures of oxygen. They considered the gas phase diffusion to be rate limiting.

Winnubst et al.²⁵ measured the time of response for an oxygen concentration change from air to oxygen for a 10 to 90% change in EMF on ZrO_2 - and Bi_2O_3 - based electrolytes. They used high gas flow rates in order to minimize the effect of gas phase diffusion on the response time of the sensor. They found that electrodes made of gold were faster than those of platinum.

Mizusaki et al.²⁸ measured the time changes in EMF after a sudden change in pressure for Pt paste electrodes for yttria-stabilized zirconia. They also found that the

response where the change was an increase in pressure was faster than the opposite experiment. A similar effect on the response time for a change from high to low or from low to high was also observed by Mogab.²⁰

Masson et al⁸ suggested that by removing the impurities of oxides of transition metals with variable valency (eg Fe_2O_3) from the electrolyte, the response of the sensor could be improved significantly. They found the response of such a sensor to rapid changes in pressure and temperature to be 7-8 times faster and concluded that the presence of Fe_2O_3 was responsible for the solubility of oxygen in stabilized zirconia.

Badwal et al.^{29,30} measured the response time of the oxygen sensors using three techniques. In the first technique, the response of the sensor to changes in oxygen partial pressures was determined by exposing the outside of the sensor to sudden changes from vacuum to air. In the second technique, a solid electrolyte disc with different electrodes on the two faces was exposed to sudden changes in gas composition from air to oxygen. The faster electrode was identified by the shape and sign of the EMF developed. In the third technique, they exposed the sensor to propane-air combustion product mixtures with varied oxygen partial pressure. They used platinum electrodes for higher temperatures and urania-scandia and platinum electrodes for lower temperatures and concluded that the sensor performance at low temperature depended strongly on the characteristics of the electrodes. At temperatures higher than 1073 K, the response of the sensor was limited by the speed of the apparatus.

Maskell³¹ has reviewed the factors which influence the speed of response of a potentiometric sensor. On changing the pressure the EMF does not change instantly

because the electrode/electrolyte interface acts as a capacitor which requires the transfer of charge. When the pressure is changed at the boundary of the electrode the potential also changes, the charge moves in and out of the double layer giving rise to the reaction [1]. Electrons are supplied by the electrode. There is an electrical resistance to this reaction and the system acts as a parallel RC combination and hence shows an RC time constant. A low electrode resistance to charge transfer would reduce the RC time constant and the response would be rapid. So the electrodes should be thin and porous with a long three phase boundary (where electrode, electrolyte and gas intersect). At longer times, there exists an equilibrium between the electrolyte and the gas represented by reaction [1]. The stoichiometry of the oxide varies with P_{O_2} . On changing the pressure, a chemical equilibrium should be established between the stoichiometry of the electrolyte and the gas phase in the double layer region and this can induce a capacitance thus delaying the response. At higher temperature, hydrodynamics in the gas phase limit the sensor response.

According to Heyne³², speed of response is adversely affected by the non-reversibility of the electrodes. For cells with good material and good electrodes, response time is of the order of milliseconds but increases to seconds or minutes when some blocking action by electrodes appears. He thought this to be the reason for the unsatisfactory performance of platinum gauze electrodes pressed on to the zirconia. He suggested that internal polarization at grain interfaces could also lead to slow or incorrect response.

According to Bannister and Hooshmand³³, sensor response depends upon three

factors, the physical limitations of the experimental apparatus, oxygen ion transfer characteristics of the sensor and the time required by the electrode/electrolyte interface to reach equilibrium. They studied the intrinsic response time of a sensor using a technique which involved a transition from vacuum to air.

Mochizuki et al.³⁴ found that the response time of zirconia oxygen sensors for steel melts was reduced considerably by optimization of the thickness of the tip end of the sensor and the amount of reference electrode powder. This reduced the immersion time of the sensor in steel melts.

1.2.4 Problems with Sensors

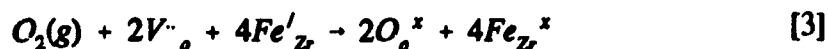
In order for a sensor to behave ideally it should obey the Nernst equation.⁸ Conduction through the electrolyte should be ionic, i.e only oxide ions should be able to move through the electrolyte. At higher temperatures (1073-1473 K) or low oxygen pressures ($< 10^{-20}$ atm)⁹, there are other conducting species such as electrons or electron holes. Due to the presence of these the ionic transport number, t_i , in the Nernst equation becomes less than one and the observed sensor output voltage is less than the theoretical, Nernstian value.^{8,35,36} The observed voltage is given by,

$$E = (1-t_e) \frac{RT}{4F} \ln \frac{P_{O_2}''}{P_{O_2}'} \quad 1.3$$

where t_e is the mean electronic transport number. Electronic transport causes a partial

short circuit of the cell. In the electrolyte, electrons move in one direction and ions move in the opposite direction to maintain electrical neutrality. The net result of this is the transfer of oxygen through the electrolyte from one electrode to another. This phenomenon, known as oxygen electrochemical semipermeability, causes a disturbance of the equilibrium at the electrodes and a change in the pressures of oxygen.³⁶ This effect is negligible below 973 K for oxygen pressures between 10^{-6} and 10 atmospheres.³⁶

Electronic conductivity is also caused by the presence of transition metal cations with variable valency, such as Fe^{2+} , in the ceramic. Fe^{3+} has a tendency to get reduced to a lower valence state which gives rise to electronic conduction. This increases the oxygen absorption capability of the ceramic surface and hence the response time of the sensor.⁷ In their study of the desorption of oxygen from calcia-stabilized zirconia (CSZ), Dou, Masson and Pacey³⁷ demonstrated that the amount of oxygen desorbed was proportional to the iron content of CSZ because the iron atoms were the trapping sites according to the following reaction,



where Fe'_{Zr} are the iron ions at the Zr sites and $\text{Fe}_{\text{Zr}}^{\times}$ are the holes trapped at these iron atoms.

At higher temperature, grain growth in the zirconia makes the sensor brittle, leading to mechanical breakage.

Oxygen sensors made of less pure zirconia electrolyte could be subject to long term EMF changes due to the presence of a second phase.^{26,38} Most of the commercial zirconia electrolytes contain SiO_2 and Al_2O_3 as impurities. These impurities segregate at

the grain boundaries thus removing the direct contact between the zirconia electrolyte grains and causing grain boundary impedance.⁹ The impurity phase is a poor oxygen ion conductor as the mobility of oxide ion in this phase is different. Transport properties in this impurity phase are different from those in the bulk phase. When the ionic transport number of the second phase is different from that of the bulk phase, then the observed EMF would be different from the correct EMF of the cell.⁹ Due to the presence of the second phase, a concentration gradient exists in the ceramic electrolyte which gives rise to an internal EMF which contributes to the overall EMF thus making the observed emf different from the correct value. The extent of this deviation depends upon the transport properties of the impurity phase and is negligible if the ionic transport number of the second phase is unity.

The performance of a sensor is degraded due to aging. In ZrO_2 -8 mol% Y_2O_3 , aging occurs gradually in the temperature range of 1173-1473 K causing a decrease in ionic conductivity.^{3,39} For sensors which operate at such a high temperature range, aging is due to defect ordering processes. On heating the sensor again at a temperature higher than 1673 K, the defects can be disordered again and the ionic conductivity is restored to its original value.³ With a decrease in grain size, the rate of aging increases. According to Carter and Roth⁴⁰, there is an order-disorder transformation near 1273 K for calcia-stabilized zirconia. Due to this ordering the resistivity increases linearly with the square root of time. The activation energy remains the same, indicating the same mechanism of ionic conduction.

A rapid heating or cooling of the cell (especially those in the form of tubes) can

cause microcracks in the electrolytes due to thermal stress. Because of porosity or microcracks in the electrolyte, molecular oxygen can pass from one electrode to the other, thus changing the partial pressure of oxygen at the two electrode/electrolyte interfaces.⁴¹ This problem can be overcome by using proper preparation and sintering techniques.

At low temperatures (below 773 K), the impedance of the cell is too high³⁶ and the response of the sensor is very slow. High cell impedance is caused by lower conductivity and attainment of thermodynamic equilibrium is difficult.⁴² For oxygen sensors with porous platinum electrodes, the impedance due to the electrode/electrolyte interface dominates the total impedance at low temperature.²³

There are a number of factors responsible for the deterioration of the electrodes with time. The electrodes can become poisoned or blocked by certain chemicals or dust and their catalytic effect is decreased.³¹ This depends upon the environment in which the sensor is used.

Thermal annealing leads to sintering and grain growth of platinum particles. At high temperatures, greater than 1073 K, grain growth in platinum reduces the surface area and porosity of the electrode thus reducing the length of the three-phase boundary, leading to slower incorporation of oxygen. Badwal et al.²³ observed that heating at 1173 K increased the resistance and the relaxation time of the electrode processes at 873 K for porous platinum electrodes on yttria-stabilized zirconia. This deterioration was said to be caused by sintering and grain growth in platinum.

Performance of the sensor is also degraded if the electrodes contain glassy

materials which block the three-phase electrochemical reaction sites (ERS).³¹

1.3 AC Impedance Technique

This technique was first introduced by Bauerle⁴³ for electrochemical studies on solid electrolytes. Using impedance data the electrochemical properties of the system can be determined and the properties due to the bulk can be separated from the interfacial properties, thus giving an insight into the factors limiting the response of the sensor.

In the impedance technique, an electrochemical system is perturbed using a sinusoidal excitation signal and the response of the system is studied over a wide range of frequencies. The excitation can be applied as an alternating voltage or an alternating current (ac). The measured response is an ac current or voltage, respectively, and the impedance of the system can be calculated. The amplitude of the voltage across the system should be small in order to have a linear relationship between the current and the voltage.⁴⁴

If $v(t)$ is a sine-wave input voltage

$$v(t) = V_m \sin(\omega t) \quad 1.4$$

then the response is often also a sine wave

$$i(t) = I_m \sin[\omega t + \phi(\omega)] \quad 1.5$$

where $i(t)$ is the current, ω is the angular frequency and $\phi(\omega)$ is the phase difference between the voltage and the current. ϕ is zero for purely resistive behaviour.

The impedance is defined as $Z(\omega) = v(t)/i(t)$. The modulus or the magnitude of

the impedance $|Z|$ is defined as $V_m/I_m(\omega)$.

The impedance, $Z(\omega)$, is a complex quantity which can be represented in cartesian or polar coordinates as

$$Z(\omega) = Z' + jZ'' \quad 1.6$$

$$Z^*(\omega) = Z' - jZ'' \quad 1.7$$

$$Z(\omega) = |Z| e^{j\phi(\omega)} \quad 1.8$$

where Z' and Z'' are the real and the imaginary parts of the impedance, respectively, j is $(-1)^{1/2}$ and Z^* is the complex conjugate of Z . The relationship between these quantities is

$$|Z| = (Z'^2 + Z''^2)^{1/2} \quad 1.9$$

$$\text{and } \phi(\omega) = \arctan(Z''/Z') \quad 1.10$$

The real and imaginary parts of the impedance are given by

$$Z' = |Z| \cos \phi \quad 1.11$$

$$Z'' = |Z| \sin \phi \quad 1.12$$

For the circuit shown in Fig. 2.3.1.1, A is the voltage across a series combination of a reference resistance R_s and system with impedance $Z^*(\omega)$ and B is the voltage across the $Z^*(\omega)$.⁴⁵ Then

$$\frac{A}{B} = \frac{R_s + Z^*}{Z^*} = \left| \frac{A}{B} \right| e^{j\phi(\omega)} \quad 1.13$$

where $|A/B|$ is the ratio of the amplitude of the two signals. The impedance of the system may be obtained by rearranging eq. 1.13

$$Z^* = \frac{R_s}{\left| \frac{A}{B} \right| e^{j\phi(\omega)} - 1} \quad 1.14$$

Taking $e^{j\phi(\omega)} = \cos \phi + j \sin \phi$, this can be written as

$$Z^* = \frac{R_s}{\left[\left| \frac{A}{B} \right| \cos \phi - 1 \right] + j \left| \frac{A}{B} \right| \sin \phi} \quad 1.15$$

Multiplying and dividing by the complex conjugate of the denominator, we get

$$Z^* = \frac{R_s \left[\left(\left| \frac{A}{B} \right| \cos \phi - 1 \right) - j \left| \frac{A}{B} \right| \sin \phi \right]}{\left| \frac{A}{B} \right|^2 - 2 \left| \frac{A}{B} \right| \cos \phi + 1} \quad 1.16$$

This can be separated into real and imaginary components.

The real part of the impedance is,

$$Z' = \frac{R_s \left[\left| \frac{A}{B} \right| \cos \phi - 1 \right]}{\left| \frac{A}{B} \right|^2 - 2 \left| \frac{A}{B} \right| \cos \phi + 1} \quad 1.17$$

The imaginary component is,

$$Z'' = \frac{R_s \left| \frac{A}{B} \right| \sin \phi}{\left| \frac{A}{B} \right|^2 - 2 \left| \frac{A}{B} \right| \cos \phi + 1} \quad 1.18$$

1.4 Method of Lissajous Figures

By using Lissajous figures the impedance of the cell can be measured down to very low frequencies. A Lissajous figure is a pattern resulting when two sinusoidal voltages of the same frequency are applied to both the horizontal and vertical inputs of an oscilloscope. This is usually in the form of an ellipse and the nature of the ellipse gives the value of the ratio of the amplitude of the two signals and the phase difference between them. At very low frequencies, an XY recorder can be used instead of an oscilloscope.⁴⁶

If a system of impedance Z is perturbed by applying a voltage

$$v(t) = V_m \sin \omega t$$

then the current through the system will be, from eq. 1.5,

$$i(t) = \frac{V_m \sin(\omega t + \phi)}{|Z|} \quad 1.19$$

When $v(t)$ is connected to the vertical plates and $i(t)$ to the horizontal plates of an oscilloscope or an XY recorder, the input and the output signals are displayed simultaneously in the form of an ellipse and the impedance parameters can be measured from its dimensions (Fig. 1.4.1).⁴⁷ The voltage ratio $|A/B| = RR'/PP'$ and the phase angle, ϕ can be calculated as $\sin^{-1} (QQ'/PP')$.

The real and imaginary components of the impedance can be calculated using equations 1.17 and 1.18.

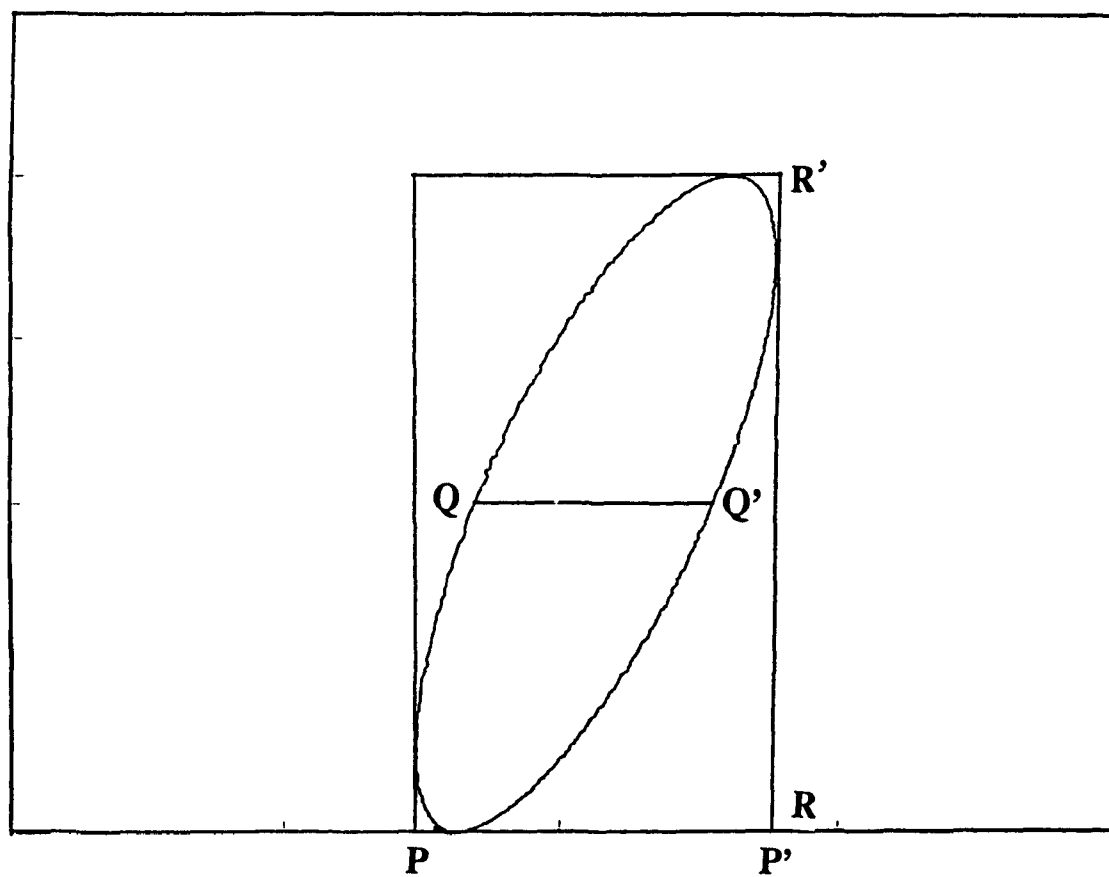


Fig. 1.4.1 A typical Lissajous figure

Impedance data can be plotted in a number of ways, in the complex admittance plane, complex impedance plane or as Bode plots. In the complex impedance plane, measurements over a large range of excitation frequencies give a set of semicircles each corresponding to processes in the bulk of the electrolyte and at the electrode/electrolyte interface. The sensor can be represented by an equivalent circuit as a parallel combination of resistance and capacitance. In a plot of the real vs the imaginary component of the impedance, the semicircle obtained at low frequencies (less than 100 Hz) usually is due to the electrodes and the semicircle obtained at higher frequency is due to the electrolyte. Sometimes a semicircle due to the presence of grain boundaries is observed between the bulk and the electrode semicircles. The frequency at the top of a semicircle, $f_{\max}$, is the relaxation frequency and obeys the relationship,

$$2 \pi f_{\max} R C = 1 \quad 1.20$$

so the time constant of the respective process is

$$\tau = (2 \pi f_{\max})^{-1} \quad 1.21$$

The contributions from various impedances can be well separated only when the relaxation frequencies are different by at least two orders of magnitude.

In actual practice, all the semicircles are not obtained at all temperatures, the ones corresponding to the bulk and the grain boundaries appear at lower temperatures and the one due to the electrodes is observed at higher temperature. The semicircular arcs obtained are usually depressed, the centre of the arc is displaced below the horizontal axis. This is supposed to be caused by the roughness of the electrodes so that the

relaxation time, τ , is not single-valued but distributed continuously or discretely around a mean value.⁴⁴ The amount by which the semicircle is depressed is related to the width of the relaxation time distribution.⁴⁴ The semicircle is only approximated by an RC time constant. Sometimes overlapping depressed semicircles are obtained which correspond to two processes occurring in series.³⁹

In order to identify the various semicircles, the following points can be considered. The semicircle corresponding to the bulk occurs at lower temperatures at high frequencies whereas the one corresponding to the electrode occurs at higher temperatures at lower frequencies. Impedance due to the bulk depends on the length of the sample so the resistance of the bulk will change proportionately on changing the length whereas the electrode resistance is independent of this parameter. The resistance due to the electrodes may depend on the partial pressure of oxygen whereas the resistance due to the bulk is independent of the pressure.³⁹

The shape of the semicircle depends on the rate-limiting process. If the electrode process is controlled by the diffusion of ions or molecules to or from the electrode/electrolyte interface, the interfacial impedance is a Warburg impedance. If Warburg impedance is present, then the shape of the impedance diagram of the electrode is that of a straight line making an angle of 45° with the axes on the high frequency part and a circular arc on the low frequency part.⁴⁸

Activation energy can be determined from the dependence of the charge transfer resistance on the temperature. Impedance data can be used to obtain a mechanism for the processes occurring at the electrode.

Bauerle⁴³ used the complex impedance technique to study the polarization behaviour of yttria-stabilized zirconia with Pt electrodes over a range of temperatures and oxygen partial pressures. The data was analysed in the complex admittance plane and three polarisations were obtained which were due to the electrodes, grain boundaries and the bulk of the electrolyte.

Using the impedance technique on calcia-stabilized zirconia, Beekmans and Heyne³⁸ investigated the effect of a second phase caused by the segregation of impurities at the grain boundaries on the electrochemical properties of the electrolyte.

Badwal et al.²³ used the complex impedance technique to show that the slow response rate at lower temperature depends on the physical and chemical nature of the electrode and the ability of the electrodes to exchange oxygen with the surroundings. They observed that the relaxation times for urania-scandia electrodes were one or two orders of magnitude shorter than those for the platinum electrodes under similar conditions.

Moghadam and Stevenson⁴⁸ discussed the application of the AC impedance technique to diffusion studies, used this technique to study the solubility and diffusion of oxygen in platinum on yttria-stabilized zirconia and suggested that the surface diffusion of oxygen on Pt was the rate-limiting step.

Wang and Nowick⁴⁵ used the impedance technique to study the kinetics for platinum electrodes on ceria electrolytes at high temperatures and pressures. They observed that the angle of depression was independent of temperature in a limited range of oxygen pressure. They suggested that the large value of the angle of depression was

due to the distribution of the circuit parameters.

Verkerk and Burgraaf⁴⁹ studied the influence of the nature of the electrodes and electrolytes on the kinetics of oxygen transfer reactions using the ac impedance technique.

Sasaki et al.⁵⁰ used this technique to study the kinetics with platinum and silver electrodes on yttria-stabilized zirconia and found that the interfacial resistance was dependent on the pressure whereas the capacitance and the angle of depression were independent of pressure and temperature.

Chu and Seitz⁵¹ studied the ac impedance of calcia- stabilized zirconia using Au and Pt electrodes over the frequency range of 100 Hz to 500 kHz at different temperatures and oxygen partial pressures. They observed three semicircles at different temperatures. The bulk and the grain boundary resistance did not show any dependence on the partial pressure of oxygen. For the electrodes, the capacitance was found to be dependent on the temperature, pressure of oxygen and the material of the electrodes.

Velle et al.⁵² used this technique to characterize Pt electrodes on yttria-stabilized zirconia. Depending on the variation of charge transfer and diffusional resistance with temperature and partial pressure, they proposed a rate-limiting step on the surface of the sensor.

Badwal et al.⁵³⁻⁵⁵ used the impedance technique extensively for electrochemical measurements at the electrode/electrolyte interface and for studies of the effect of temperature, oxygen pressure and electrode microstructure and composition. They found that the relaxation time (which determines the inherent response of the sensor to the

establishment of O_2/O^{2-} equilibrium between gas, electrode and electrolyte) to be two orders of magnitude lower for the urania-scandia electrodes.

Schouler and Kleitz⁵⁶ used this technique to study the capacitive effect at an oxygen-silver-stabilized-zirconia interface.

1.5 Studies of Microstructure using a Scanning Electron Microscope

A scanning electron microscope study of the electrolyte and electrode helps in understanding the changes in electrical properties thereby strengthening the understanding of the mechanism of the reactions on the surface.

The morphology of the electrode is characterized by the surface area of the electrode/electrolyte, gas/electrolyte and gas/electrode interfaces and the length of the three- phase line.

Using scanning electron micrograph studies, Pizzini et al.⁵⁷ studied the influence of high temperature annealing and heavy current treatments on porous platinum electrodes and demonstrated that both the structure and catalytic activity of the electrodes is influenced by these treatments. They thought that the heavy current treatment increased the number of active spots on the surface of Pt where oxygen was adsorbed and dissociated.

Verkerk et al.⁵⁸ have used scanning electron micrographs (SEM) to compare the morphology of Pt sputtered and gauze electrodes. They measured the ratios of the

electrode areas, the three-phase line lengths, the electrode/electrolyte contact area, the electrolyte/gas contact area and the electrode/gas contact area and observed that with Pt sputtered electrodes, the three phase line length was three orders of magnitude greater and the electrode/electrolyte area was 16 times greater than with the gauze.

Badwal et al.²³ and Badwal⁵³ have used this technique to study the effect of heat treatment at various temperatures on the microstructure of Pt, Au, Ag and $(U_{0.5}Sc_{0.5})O_{2\pm x}$ electrodes on YSZ. They observed that heating the Pt electrodes at 1173 K caused reductions in the fine electrode porosity, the total electrode/electrolyte contact area, the extent of the three-phase contact region and the isolation of Pt particles. Heating at 873 K caused the deterioration of the Ag electrode and heating at 1173 K caused the metal particles to become isolated. For urania-scandia electrodes, the electrolyte/electrode contact area was improved on heating.

Using microprobe analysis, Beekmans and Heyne³⁸ studied the composition of a second phase in some samples of calcia-stabilized zirconia and correlated this to the electrical and electrochemical behaviour of the sensor. The amount and composition of the second phase determined whether a particular sample was suitable for electrochemical application.

Chu and Seitz⁵¹ used this technique to measure the effect of sintering temperature on the grain size of calcia-stabilized zirconia.

Based on SEM pictures, Braunshtein et al.⁵⁹ suggested that the heating rate was very important for the electrode resistance. If heated too fast, the Pt tends to form separate islands and this increases the impedance of the sample.

Wang and Nowick⁶⁰ used the SEM micrographs to observe the effect of aging on Pt paste electrodes on ceria-based electrolytes.

Krafthefer et al.⁶¹ used SEM to study the physical changes on the surface of Pt electrodes after 4000 h of operation at 873 K. They observed that aging effects were less with a smaller grain size of platinum and better adherence to the electrolyte.

1.6 The Mechanism of Oxygen Transfer in the Sensors

The rate at which the electrodes come to equilibrium after a change in the concentration of oxygen depends on the mechanism of the overall reaction. Many studies have been performed on the electrode processes. However, the rate-limiting elementary step is still unknown. In most studies in the literature, the measurements were made under different experimental conditions, so no comparison is possible.

The rate-limiting step can be identified by studying the dependence of electrode resistance, response time, limiting current or exchange current on the temperature, the partial pressure of oxygen, the flow rate of the gases and the structure of the interface.

The various possible elementary steps for the oxygen exchange reaction on the surface of the sensor are,^{62,43}

1. Diffusion of holes across the electrode/electrolyte interface or inside the electrolyte
2. Diffusion of O^{2-} inside the electrolyte.
3. Oxidation of O^{2-} to singly charged O^- at the electrochemical reaction site (ERS)
4. Oxidation of O^- to O atoms at the ERS

5. Diffusion of two O atoms to a recombination site
6. Recombination of two O atoms at the ERS
7. Desorption of O₂ from the surface
8. Dissolution and diffusion of O or O₂ into Pt
9. Diffusion of molecular oxygen in the gas phase or in the pores of Pt
10. Flow of the gas through the solenoid

Any one or more of these steps could be rate-limiting. Some of these processes could occur on the electrode-gas interface, electrode-electrolyte interface, electrolyte-gas interface or the electrode-electrolyte-gas three phase boundary.

Bauerle⁴³ found that the electrode resistance depended on preparation, temperature and oxygen partial pressures. He found that the resistance for porous electrodes was low and was proportional to $P_{O_2}^{-0.64}$. He found that the temperature dependence of the electrode resistance corresponded to a thermally activated process with an activation energy of 200-240 kJ mol⁻¹ and suggested that this could not correspond to the adsorption step as the temperature dependence was in the opposite direction and thought that either the molecular dissociation step or the electron transfer step could be rate limiting. The electrolyte resistance did not show any dependence on the pressure.

Pizzini⁶² suggested that the previous history of the electrode is very important in determining the kinetic behaviour. He suggested that if the electrolyte thickness is small (0.1 cm) the fastest step over a large range of temperatures is the gas-phase diffusion. For Pt paste electrodes on yttria-stabilized zirconia, he observed that, over a limited pressure range, the electrode resistance was proportional to the square root of the

partial pressure of oxygen, indicating that the rate-limiting step was proportional to the concentration of atomic oxygen adsorbed on the walls of the pores. At very low pressures, the electrode resistance was inversely proportional to the pressure of oxygen. Based on the pressure and temperature dependence of the electrode resistance below and above 973 K, he concluded that the surface diffusion of oxygen is the rate limiting step below 973 K and the surface dissociative chemisorption is limiting above 973 K.

Verkerk and Burgraff^{49,58} suggested that the electrode process is strongly influenced by the nature of the electrolyte. Using Pt gauze and sputtered electrodes on three different electrolytes, they suggested that the rate-limiting step was the diffusion of atomic oxygen on the surface of platinum for zirconia- and ceria- based materials whereas diffusion on the surface of the electrolyte was rate-limiting for bismuth oxide-based materials. They observed that the electrode resistance was not influenced by the grain size of the electrolyte.

According to Badwal et al.³⁰, both the three-phase gas-electrode-electrolyte boundary and the electrode/gas contact area influence the oxygen exchange reaction at porous platinum electrodes.

Wang and Nowick⁶⁰, Okamoto et al.⁶³ and Sasaki et al.⁵⁰ observed an order of $\frac{1}{4}$ for the dependence of resistance on the partial pressure of oxygen in the lower pressure region. They said that the rate-limiting step was charge transfer at low coverage. According to Wang and Nowick, the electrode process is limited by charge transfer if the electrode resistance varies as $P_{O_2}^{\frac{1}{4}}$ or $P_{O_2}^{-\frac{1}{4}}$.

Based on response time measurements, varying the gas composition at a constant

total pressure, Anderson and Graves²⁷ suggested that diffusion in the gas phase was rate limiting.

Gur et al.⁶⁴ observed that for platinum electrodes on scandia-stabilized zirconia, the limiting current at low overvoltages showed a weak negative dependence on the pressure of oxygen at temperatures of 773 and 873 K but was dependent on the quarter power of the partial pressure of oxygen at temperatures above 873 K. They suggested that gaseous diffusion limited the currents at high overvoltages.

Winnubst et al.²⁵ proposed that the response was controlled by gaseous diffusion at times less than 0.5 s.

Robertson and Michaels⁶⁵ observed that for Pt paste electrodes on yttria-stabilized zirconia at 873 K and a pressure of 0.21 atm, anodic limiting currents were independent of the partial pressure of oxygen and cathodic limiting currents were proportional to the square root of the pressure of oxygen.

1.7 Purpose

The overall purpose was as follows:

1. To study the mechanism of oxygen exchange reaction on the surface of the sensor and find the rate limiting step.
2. To find the reason for the faster response of the sensor when the partial pressure of oxygen in contact with the sensor changed from low to high than when it changed from high to low. Such experiments have been done by other authors^{22,25,27,28} but the results

have not been explained clearly.

3. To study the properties due to the bulk and the interface of the sensor.
4. To observe the effect of construction of the electrode on the response of the sensor.
5. To find whether the RC time constant obtained from AC impedance technique was equal to $t_{0.63}$ from the technique where the partial pressure of oxygen is suddenly changed.

EXPERIMENTAL

2.1 Preparation of the sensors

Two sensors, A and B, which differed in the construction of their inner electrode, were prepared.

The green sensor bodies were prepared by the method of slipcasting, using TOSOH zirconia powder. The composition of the zirconia powder as quoted by the manufacturer is given in Table 2.1.1.

The molds used were made from plaster of Paris. The form consisted of two equal halves of an elongated cylinder 30 cm long and 8 cm diameter. A depression in the form of a test tube was made in the centre of the mold. The two parts of the mold could be joined together with two or three clamps.

A slurry was prepared by mixing 200 grams of zirconia powder with 80 mls of distilled water and blending in a blender (Osterizer 10) at high speed for 2 minutes. The air bubbles were removed from the slurry by placing the beaker containing the slurry in a dessicator connected to a vacuum pump and degassing for 2 minutes. The resulting slurry was then poured into the plaster of Paris molds and, after waiting for 1.4 minutes, the part of the slurry which had not stuck to the mold was poured out. Then these molds

Table 2.1.1 Composition of the TOSOH zirconia powder used for making sensors A and B

Grade : TZ-8Y

Lot No. : Z 808686 P

1. Chemical Analysis

Y_2O_3 = 13.50 wt %

Al_2O_3 < 0.005 wt %

SiO_2 < 0.002 wt %

Fe_2O_3 = 0.004 wt %

Na_2O = 0.026 wt %

Ig. loss = 0.82 wt %

2. Crystalline size 247×10^{-8} cm

3. Specific Surface Area $14.9 \text{ m}^2 \text{ g}^{-1}$

were kept intact for 1 hour after which they were carefully opened and the green sensor bodies were taken out. Their edges were then scraped with a blade. These sensor bodies were shaped like test tubes 20-23 cm long, 1.3 cm o.d and 1.0 cm i.d.

The green sensor bodies thus formed were air dried and put in a furnace (Keith, Model MPC 08) for firing. The sensor bodies were covered on all the sides with alumina beads to avoid bending. The sensor bodies were then sintered at 1550°C according to pattern 1 (shown in Fig.2.1.1). According to this pattern, the temperature of the furnace was raised at the rate of 120°C/hour till it reached 1550°C, it was maintained the same for three hours and then was lowered at the rate of 200°C/hour to room temperature.

Pure platinum wire (diameter 0.51 mm) was wrapped around the closed end of the sintered sensor body three times and tied. Platinum paste (E 8300, supplied by Johnson Matthey, Material Technology, U.K) was then applied on the inside and outside of the closed end of the sensor, thus making a connection between the ZrO₂ and Pt wire. After warming the sensor in the drying oven at 100° C for 10 minutes, the sensor was again put in the furnace for the fusion of the Pt paste with the Pt wire and ZrO₂ according to pattern 2 (shown in figure 2.1.2). According to this pattern, the temperature of the furnace was raised at the rate of 50°C/hour for 10 hours and then at the rate of 100°C/hour for 8 hours until it reached 1300°C, maintaining the same temperature for 1/2 hour and again lowering the temperature at the rate of 200°C/hour to room temperature.

The sensors thus formed were about 15 cm long with an o.d. of about 0.95 cm and i.d. of about 0.75 cm. The percentage shrinkage in the dimensions of the sensor

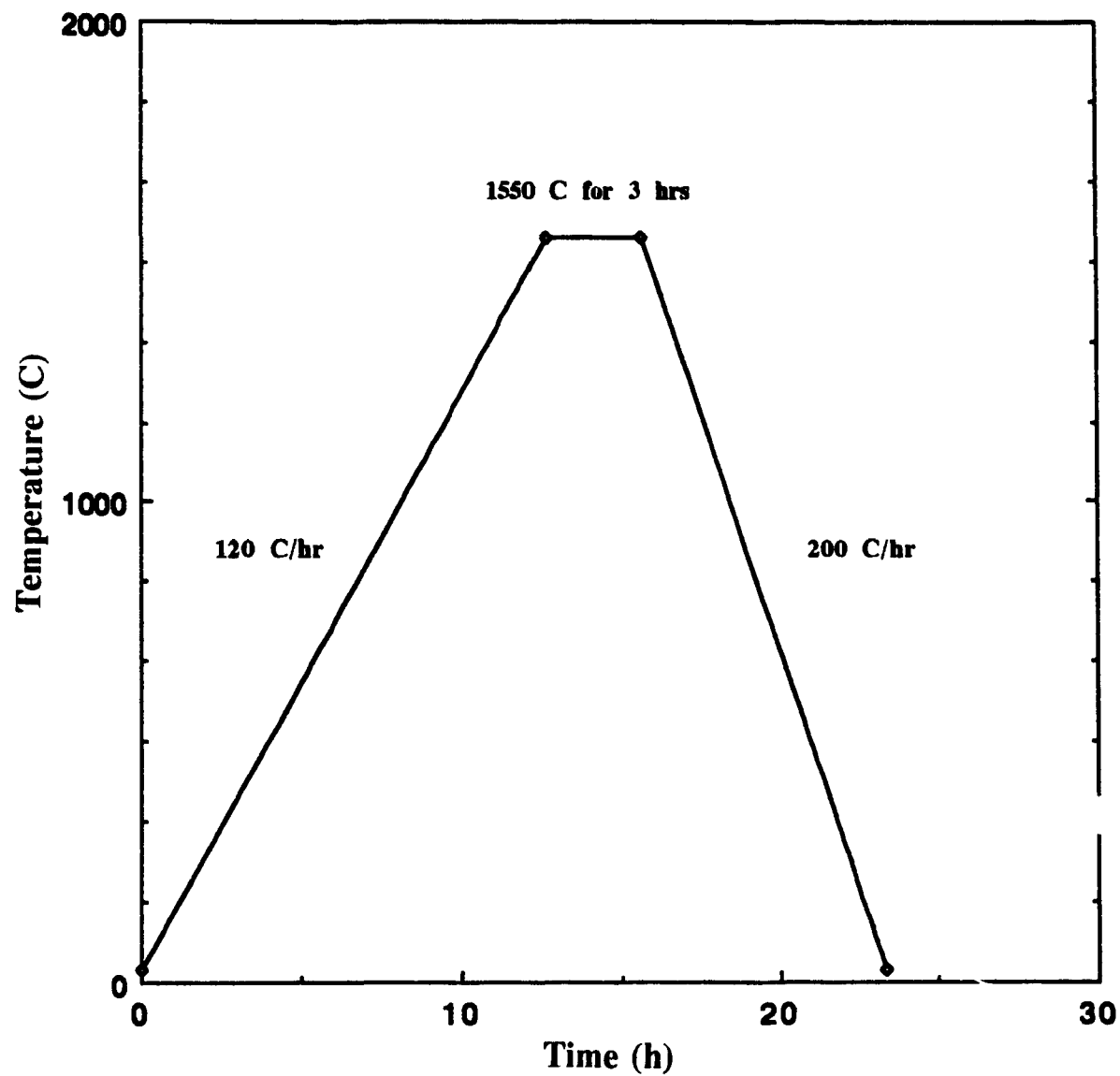


Fig. 2.1.1 Green body sintering temperature profile according to pattern 1 on the furnace

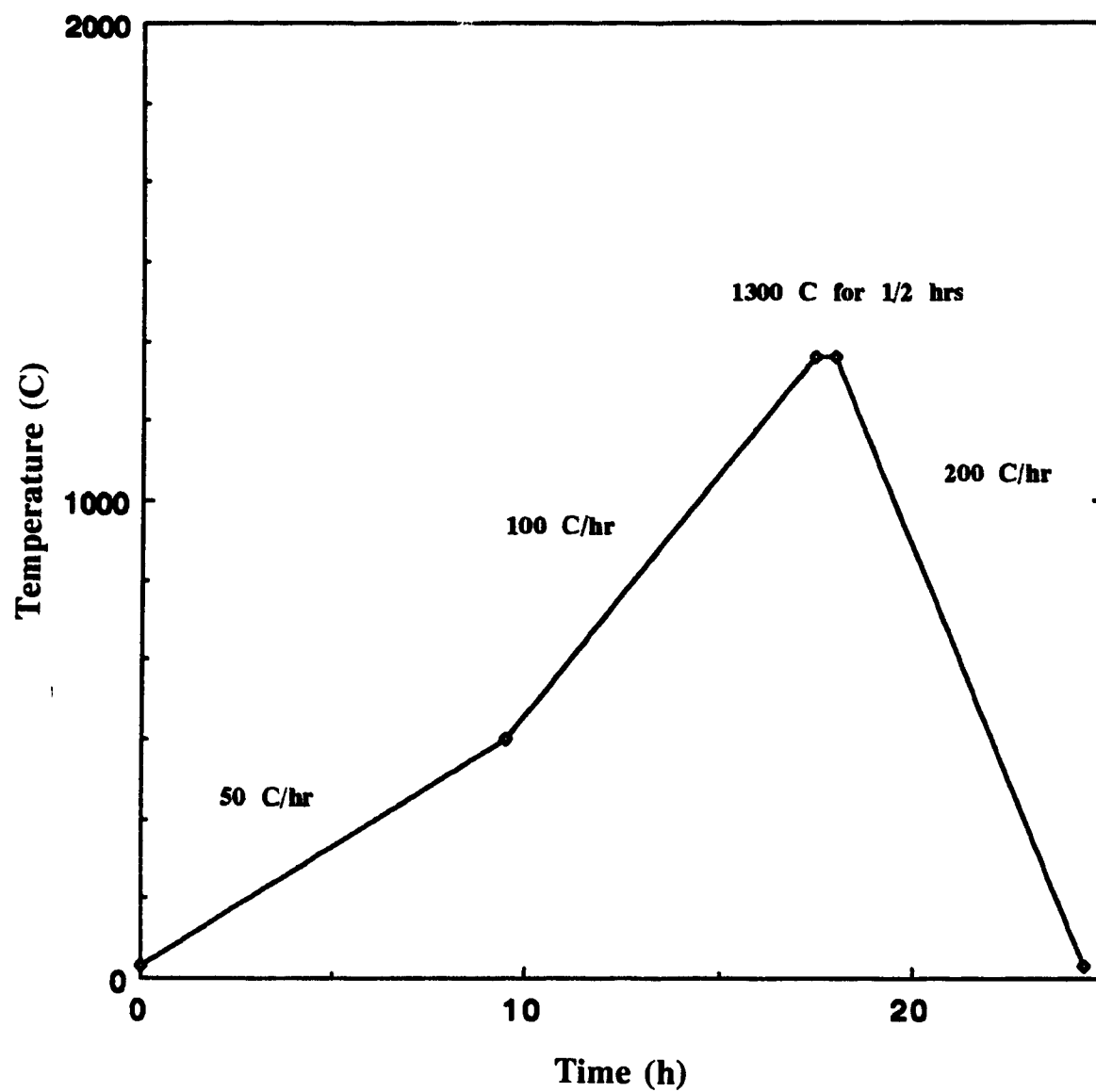


Fig. 2.1.2 Platinum paste adhesion profile according to pattern 2 on the furnace

due to sintering varied between 26% and 29%.

For sensor A, a platinum wire mounted on an alumina tube was pressed onto the Pt paste on the inside of the sensor thus making the inner lead. For sensor B, in addition, platinum gauze was pressed between the platinum paste and inner lead.

2.2 EMF Measurements

2.2.1 Apparatus

Figure 2.2.1.1 gives the schematic diagram of the apparatus used for measuring the EMF of the sensor following a sudden change of the partial pressure of oxygen. The apparatus consisted of two parts, A and B. Part A could be isolated from part B using a fast acting solenoid valve S (MKS Control valve, Type 0248 A-50000 SV or ASCO Red Hat Valve, type 8262G90 VM).

The furnace used for heating the sensor consisted of a quartz tube wrapped in asbestos paper with a nichrome wire winding on the outside. Aluminium oxide (Alundum) paste was applied on top of that. A brass tube was placed inside the quartz tube to ensure even heating. The furnace could be heated up to 950 K.

Almost three quarters of the sensor extended into a Pyrex tube (later replaced by a quartz tube for working at higher temperatures) which was placed inside the furnace. A thermocouple (Pt, Pt-13%Rh, type R), touching the outside of the closed end of the sensor, was connected to the temperature controller (Omega, Auto tune model CN 7000).

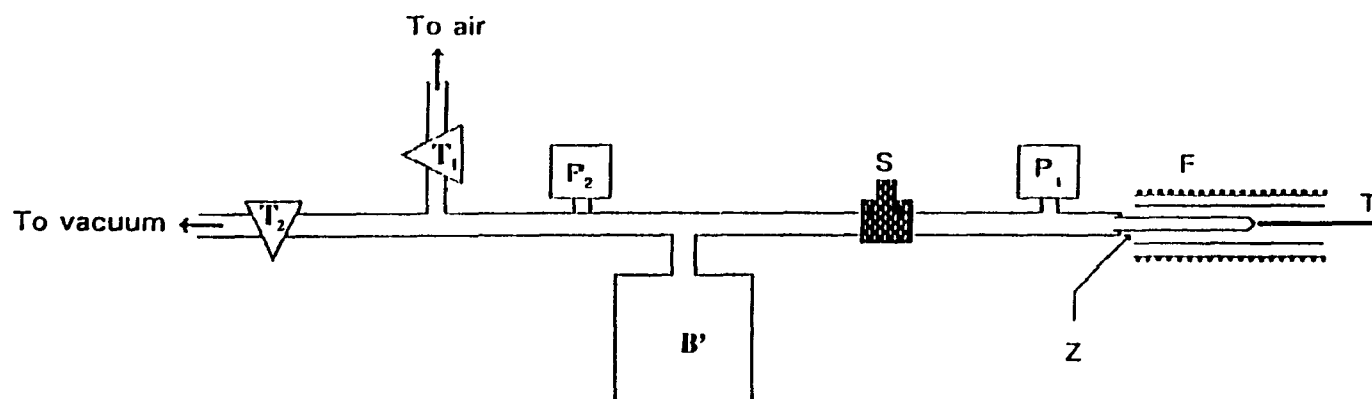


Fig 2.2.1.1 Schematic diagram of the apparatus used for the EMF measurements. B', expansion bulb; F, furnace; P₁, P₂, pressure transducers; S, solenoid valve; T, thermocouple; T₁, T₂, valves; Z, zirconia oxygen sensor.

Two LED displays on the temperature controller indicated all controller parameters as well as process temperature and set point value. The required temperature was set on the temperature controller using the front panel touch button switches. The temperature of the furnace could be controlled to an accuracy of $\pm 1^{\circ}\text{C}$.

A pressure transducer, P_1 (MKS Baratron, type 122AA-01000 AB), was connected to part A of the system through an O-ring seal. The pressure transducer output was read on the Hewlett Packard multimeter (model 3468) set at the VDC setting. For reading low pressures, a pressure transducer with a range 0-10 torr was used and for reading high pressures, it was replaced by a pressure transducer with a range 0-1000 torr.

The pressure in part B of the system was measured using the pressure transducer P_2 (Bell & Howell, type 4-366-0006-03MO, range 0-15 psi). The pressure transducer reading was noted from the Dana digital multimeter (model 4200). This pressure transducer was calibrated against the atmospheric pressure for each experiment. Calibration of the pressure transducer was done by recording its output readings corresponding to a vacuum and to the atmospheric pressure. The atmospheric pressure was read from a barometer (Taylor). A vacuum system with a liquid nitrogen trap and a rotary pump was connected for evacuation.

The sensor output voltage was fed into the pen recorder (Fisher, model FS01W6D) or an oscilloscope (Tracor Northern digital signal averager NS-570) through a high impedance interface ($10^{12} \Omega$).

When the sensor was not in use, it was left inside the furnace in the same position at room temperature.

2.2.2 Experimental procedure

Two kinds of experiments were performed. In the first kind of experiment, air was let in by opening T_1 , keeping T_2 closed and S open. The pressure transducer P_2 gave the pressure of air inside the system, which was noted from the Dana digital multimeter. This was considered to be the initial pressure P_i . Then, after closing the valve T_1 and solenoid valve S , part B of the apparatus which also contained bulb B' was evacuated by opening the valve T_2 . The pressure transducer reading was read again, corresponding to a vacuum. T_2 was closed and the solenoid valve S was opened. A sudden change in pressure was observed as air from part A of the system rushed outside to part B. The pressure transducer reading was read again. This was taken to be the final pressure, P_f . At the same time, the sensor output was recorded on the pen recorder for the first few experiments and on the oscilloscope for the other experiments. A trace was observed for sensor output voltage as a function of time. After observing the trace on the oscilloscope, the trace could be printed on the recorder attached to the oscilloscope.

In the second kind of experiment, T_1 was closed, S was opened and parts A and B of the system were evacuated by means of a rotary pump. The valve T_2 was closed and the initial pressure P_i was read as in the previous experiments. Then the solenoid valve, S , was closed and valve T_1 was opened to let in the air at atmospheric pressure. After introducing the air, T_1 was closed and the solenoid was opened. The air from part B of the system rushed to part A and a sudden increase in pressure was observed. The final pressure P_f was recorded and at the same time the voltage vs time curve was obtained

on the pen recorder.

Some experiments were performed by introducing air at different pressures, thereby changing the initial partial pressure of oxygen from 152 torr to 5 torr at 773 K. P_i , P_f and the voltage vs time trace were recorded for each initial pressure of oxygen. Three series of experiments of this kind were done, with bulb B' of different sizes, i.e 2 litres, 100 mls, 2 mls.

Some experiments were done at higher temperatures. The temperature of the furnace was varied from 773 K to 948 K and the voltage vs time curves were obtained on the oscilloscope.

Experiments were done in which the size of the bulb B' was changed. Bulbs of 2 litres, 1 litre, 500 mls, 250 mls, 100 mls, 50 mls, 25 mls and 2 mls were used for experiments at 773 K, 823 K, 848 K, 898 K, 923 K and 948 K and the curves of voltage vs. time were obtained on the oscilloscope.

In order to confirm that the pressure change in the experiment occurred fast compared to the change in sensor output, an experiment was done in which the change of pressure from the initial to the final was observed with respect to time. The time required by the pressure to change by 90% of its final value was observed to be 24 ms.

2.3 Impedance measurements

2.3.1 Apparatus

The complex impedance measurements were performed in the frequency range from 0.001 Hz to 2 MHz. Fig.2.3.1.1 shows the schematic diagram which is similar to the one described by Wang and Nowick.⁴⁵ A sine wave generator, S (Wavetek model 650), of variable amplitude and frequency was used as a power source and was connected in series to the sensor through a reference resistance, R_s . A carbon resistor ($\pm 1\%$) or a combination of carbon resistors was used as the reference resistance. The sensor was connected directly in parallel to the detector for some initial experiments and through a high impedance interface ($10^{12} \Omega$) for the later experiments. For the high frequency measurements from 1 Hz to 2 MHz, a gain phase meter (HP 3575 A) was used to detect the voltage and the phase shift. Channel A on the gain phase meter measured the voltage across the series combination of reference resistance and sensor and channel B measured the voltage across the sensor and the phase difference, ϕ , between the two signals. The gain phase meter also measured the amplitude ratio, B/A , in decibels between the two signals. The input resistance of the gain phase meter was $1 \text{ M}\Omega$ and the input capacitance was 30 pF.

For the impedance measurements at low frequencies, an oscilloscope (Philips PM 3302) was used as a detector for initial experiments and an XY recorder (HP 7090 A) for later experiments. Output from the sensor was connected to the horizontal plates and from the sinewave generator was connected to the vertical plates of the oscilloscope. Similarly, input and output signals were connected to the X and Y axes (channel 1 and 3, respectively) of the XY recorder through a high impedance meter. The XY recorder had an input impedance of $1 \text{ M}\Omega$ shunted by 45 pF. The voltage ranges of the X and Y

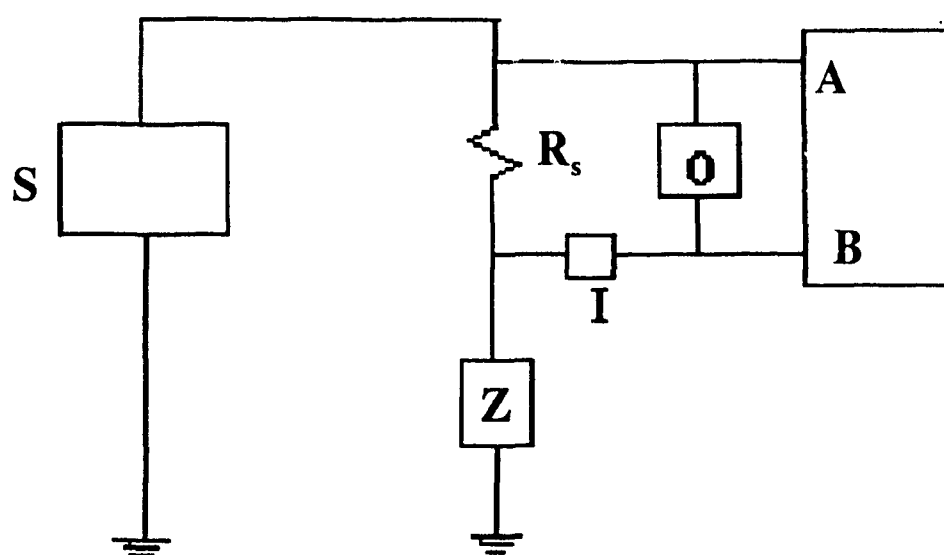


Fig 2.3.1.1 Schematic diagram for the measurement of the impedance. S, sine wave generator; R_s , carbon resistance; O, oscilloscope; A B, gain phase meter or XY recorder; I, high impedance interface, Z, zirconia oxygen sensor.

axes could be selected by changing the setup conditions. An LCD display on the front of the recorder could be used to read the voltage across channel 1 or 3.

2.3.2 Experimental Procedure

To start an experiment, the sensor was placed inside the furnace at a certain temperature. A thermocouple (Pt-13%Rh) touching the closed end of the sensor was used to measure the temperature.

A low amplitude sinewave excitation at a particular frequency was applied to the sensor and the reference resistance in series. The voltage across the sensor was always kept below 30 mV to avoid non-linearity in the relationship between the current and the voltage. This was done by adjusting the amplitude of the sinewave from the generator and/or by using an appropriate value of the reference resistance depending upon the excitation frequency. The input and output signals could be monitored on the oscilloscope to ensure their quality. The amplitude of the input signal in dB was observed on channel A and that of the output signal on channel B. The phase shift and the amplitude ratio were also observed on channel B.

For low frequency measurements, a combination of the input and output sinewaves was observed as a Lissajous figure on the oscilloscope or XY recorder. By adjusting the amplitude/div switch on the oscilloscope, the dimensions of the ellipse could be changed to give it a suitable shape.

Impedance measurements were also performed on a dummy cell which consisted

of a parallel combination of a known carbon resistance ($500\text{ k } \Omega$) and capacitance ($1 \times 10^{-6}\text{ F}$).

2.4 Scanning Electron Microscope Observation of Platinum Electrodes

The microstructure of the platinum paste on sensor A was observed by means of a JEOL (Type JXA-35) scanning electron microscope. In order to observe the outer electrode of the sensor, a small portion (about 1.5 cm) of the sensor near the closed end was cut and observed under an optical microscope and the scanning electron microscope.

To observe the structure of the platinum paste on the inside of the sensor, the small portion was again cut into two halves. A thin film of Au was deposited on top by sputtering in order to make the surface conductive.

A small piece of platinum paste on the outside of the sensor was removed and mounted on a brass platform. The SEM pictures for all the above specimens were taken at three or four different magnifications of X500, X1000, X2400 and X10000.

RESULTS

3.1 Response Time Measurements on Sensor A

Figure 3.1.1 shows a typical sensor output voltage-time trace obtained on the chart recorder for the experiment in which the pressure in contact with the inside of the sensor changed from high to low at 773 K. The sensor voltage was steady when the solenoid valve was closed. On opening the solenoid valve, the pressure on the inside of the sensor suddenly dropped to its final value, P_f . With this sudden change in pressure, the sensor output voltage changed rapidly at first and then slowly reached near its theoretical value given by the Nernst equation.

Figure 3.1.2 shows a sensor output voltage-time curve obtained on the chart recorder for an experiment when the pressure on the inside of the sensor changed from low to high at 773 K. For this experiment, opening the solenoid caused a sudden jump in pressure on the inside of the sensor.

The theoretical values of the changes in voltage were calculated using the Nernst equation,

$$\Delta E = \frac{RT}{4F} \ln \frac{P_f}{P_i} \quad 3.1$$

where P_i is the initial pressure and P_f is the final pressure in the experiment.

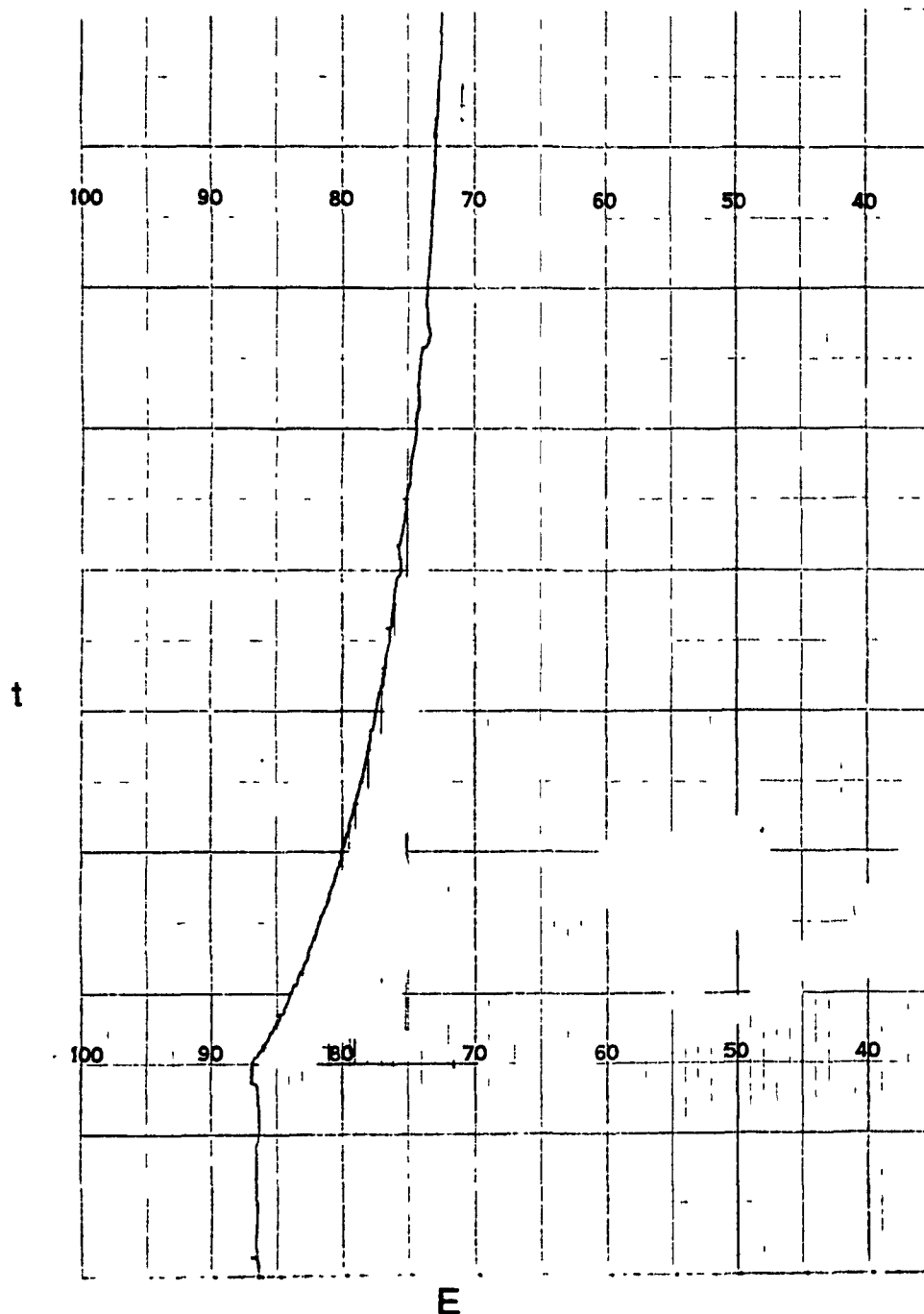


Fig 3.1.1 A trace obtained on the chart recorder of sensor output voltage with respect to time for a pressure change from 761 torr to 8.3 torr at 773 K. On the horizontal axis, one small chart unit equals 5 mV and on the vertical axis, one big chart unit equals 12s.

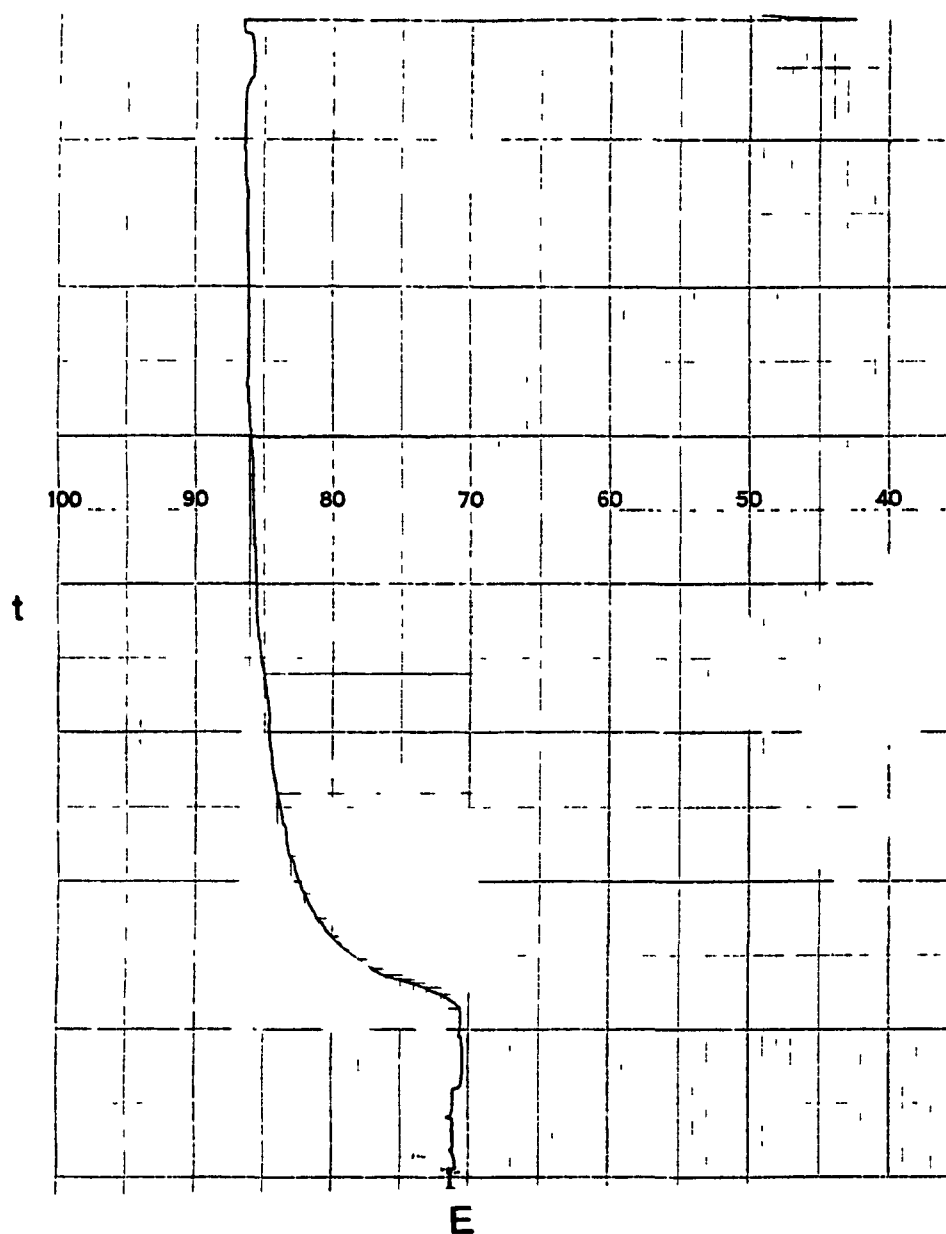


Fig 3.1.2 A trace obtained on the chart recorder of sensor output voltage with respect to time for a pressure change from 8.2 torr to 761 torr at 773 K. On the horizontal axis, one small chart unit equals 5 mV and on the vertical axis, one big chart unit equals 12s.

From the voltage-time curves, the response times, $t_{1/2}$, were measured. This was the time required by the sensor to change its voltage by half the theoretical Nernstian value. $t_{1/2}$ was taken as the response time as it gave a better reproducibility at a particular time than $t_{0.1}$ or $t_{0.9}$. For some initial experiments at 773 K and later experiments at higher temperatures, the final voltage on the trace was observed to reach near the theoretical value. The absolute mean percentage difference between the experimental and theoretical values at 773 K was 3.1 ± 2 and at higher temperatures was 1.7 ± 1.4 . In most cases the trace was terminated before the final voltage was obtained. In all the Tables, t_t is the time when the trace was terminated and ΔE_t is the experimental value of the voltage at that time.

Generally the value of $t_{1/2}$ for the p-jump experiments was less than for the p-drop experiments. For the experiment in which the pressure on the inside of the sensor changed from 760 torr to 8 torr, the response time, was found to be 22 ± 1 seconds at 773 K. For the experiment in which the pressure inside of the sensor was changed from 8 torr to 760 torr, the response time was found to be 3.9 ± 0.3 seconds at 773 K. Quoted values and uncertainties throughout the thesis are the means and standard deviations, respectively.

Figure 3.1.3 shows the sensor output voltage-time curve obtained on the oscilloscope at 873 K. The change in sensor output voltage was faster with increase in temperature. The value of $t_{1/2}$ was 0.32 s.

Tables 3.1.1, 3.1.2 and 3.1.3 show the effect of initial pressure on the response time at 773 K for experiments in which the pressure in contact with the inside of the

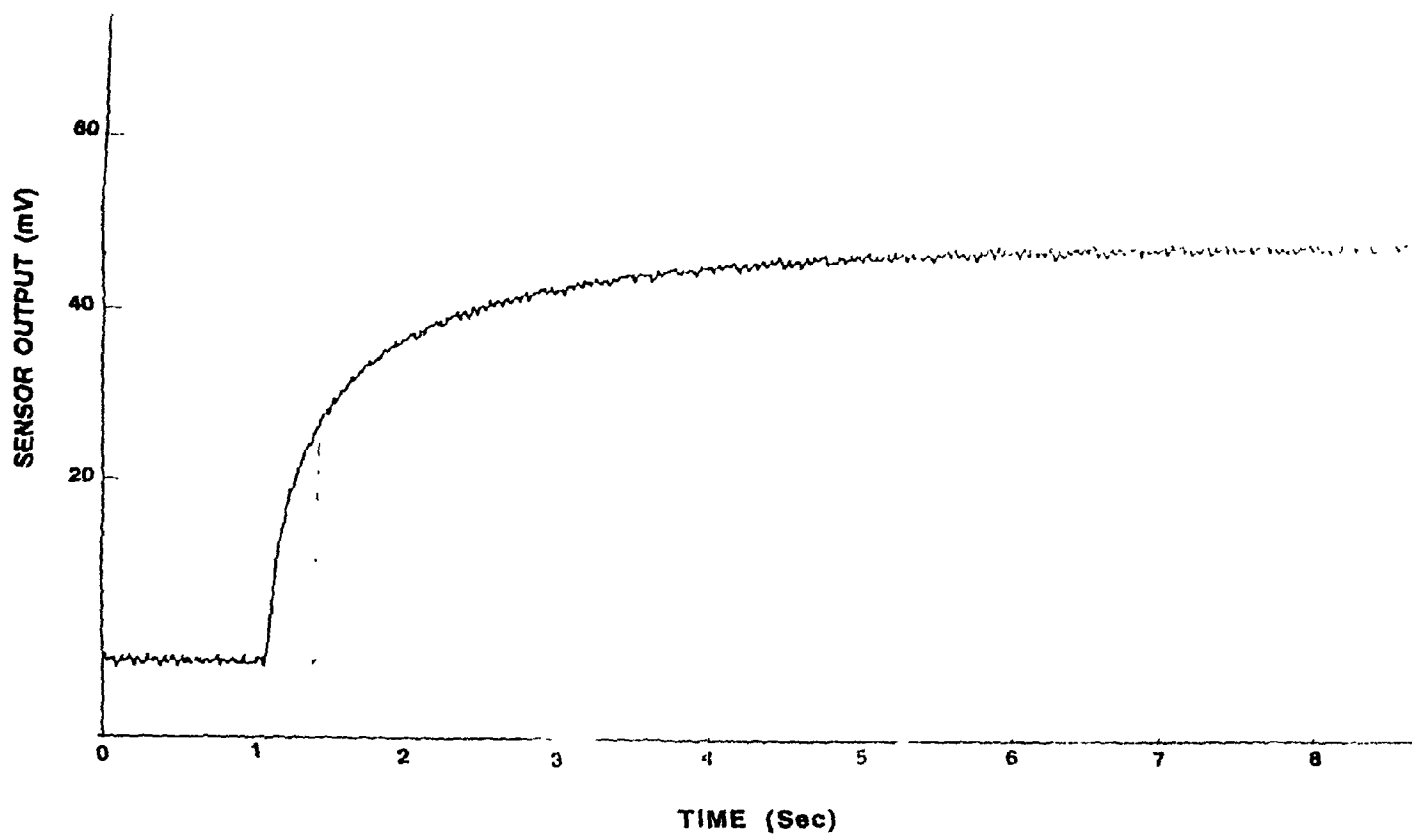


Fig 3.1.3 A trace obtained on the oscilloscope of sensor output voltage with respect to time for a pressure change from 757 torr to 52.2 torr at 873 K.

Table 3.1.1 Effect of P_i on $t_{1/2}$ at 773 K for P_i/P_f about 125

P_i (torr)	P_f (torr)	ΔE , theo (mV)	ΔE_r , (mV)	t_f (s)	$t_{1/2}$ (s)
759	5.93	80.8	70.0	190	48
652	4.87	81.5	67.5	200	51
610	4.65	81.2	65.0	173	58
582	4.22	82.0	70.0	283	62
506	4.28	79.5	67.5	195	51
475	3.45	82.0	65.0	173	60
469	3.7	80.4	65.0	180	62
402	3.07	81.2	69.0	202	56
386	2.92	81.3	70.0	198	60
264	2.06	80.8	62.5	192	70
264	2.36	78.6	60.0	182	68
216	1.77	80.0	62.5	198	71
179	1.96	75.2	60.0	247	78

Table 3.1.2 Effect of P_i on $t_{1/2}$ at 773 K for P_i/P_f about 23

P_i (torr)	P_f (torr)	ΔE , theo, (mV)	ΔE_r , (mV)	t_r (s)	$t_{1/2}$ (s)
758	33.2	52.0	45.0	137	34
597	26.1	52.1	40.5	154	37
501	22.0	52.0	45.0	149	39
412	18.0	52.2	42.5	158	42
337	14.8	52.0	45.0	126	43
327	14.2	52.2	42.0	167	50
274	11.9	52.3	45.0	176	44
267	11.7	52.0	41.0	154	49
202	8.9	52.0	45.0	149	45
209	9.2	52.0	45.0	173	45
158	6.8	52.4	40.0	156	48
131	5.6	52.3	38.0	132	54
125	5.3	52.5	40.0	140	66
74	3.3	52.0	45.0	190	60
44	2.1	50.9	42.5	210	63

Table 3.1.3 Effect of P_i on $t_{1/2}$ at 773 K for P_i/P_r about 14

P_i (torr)	P_r (torr)	ΔE , theo,(mV)	ΔE_r , (mV)	t_r (s)	$t_{1/2}$ (s)
755	48.8	45.6	36.5	153	57
754	48.9	45.5	33.5	140	47
666	42.9	45.7	28.0	98.4	58
611	39.5	45.6	31.5	122	50
489	31.5	45.7	35.0	140	53
462	30.2	45.5	32.0	177	70
365	23.4	45.7	30.0	158	75
289	18.9	45.5	31.0	200	77
228	14.6	45.8	28.0	108	66

sensor changed from high to low. The size of the bulb B' for these Tables was 2 l, 100 ml and 2 ml, respectively, giving a different value of P_i/P_f each time the bulb B' was changed. It was observed that the response time increased with a decrease in initial pressure. In Fig. 3.1.4, the logarithm of $t_{1/2}$ was plotted against the logarithm of P_i at 773 K for the 2 l bulb size. The slope was determined by the method of least squares and was -0.28 ± 0.04 . In Fig. 3.1.5, the logarithm of $t_{1/2}$ was plotted against the logarithm of P_i for bulb sizes of 100 ml and 2 ml. Tables 3.1.4, 3.1.5 and 3.1.6 show the variation of $t_{1/2}$ with P_i at 823 K, 873 K and 923 K, respectively. At these higher temperatures, the response time increased with a decrease in the value of the initial pressure but the change was less significant. In Fig. 3.1.6, the logarithm of $t_{1/2}$ was plotted against the logarithm of P_i at 823 K, 873 K and 923 K. The slopes in Figs. 3.1.4, 3.1.5 and 3.1.6 were obtained using the method of linear regression⁶⁶ and are reported in Table 3.1.7. It can be seen that the order of the response time with respect to pressure was about $-1/4$ at 773 K for all the bulb sizes and decreased at higher temperatures.

Table 3.1.8 shows the effect of P_i on $t_{1/2}$ 773 K for the experiments in which the pressure in contact with the sensor changed from low to high. It was observed that the response time decreased slightly with decrease in pressure. In Fig. 3.1.7, the logarithm of $t_{1/2}$ was plotted against the logarithm of P_i and the slope was found to be $+0.19 \pm 0.04$. The slope obtained in this experiment was positive which is reverse to that of the p-drop experiment. From Table 3.1.8, it can be seen that the ratio P_i/P_f changed with a change in the initial pressure as the final pressure was always close to 1 atm.

The response time of the sensor was measured as a function of temperature for fixed

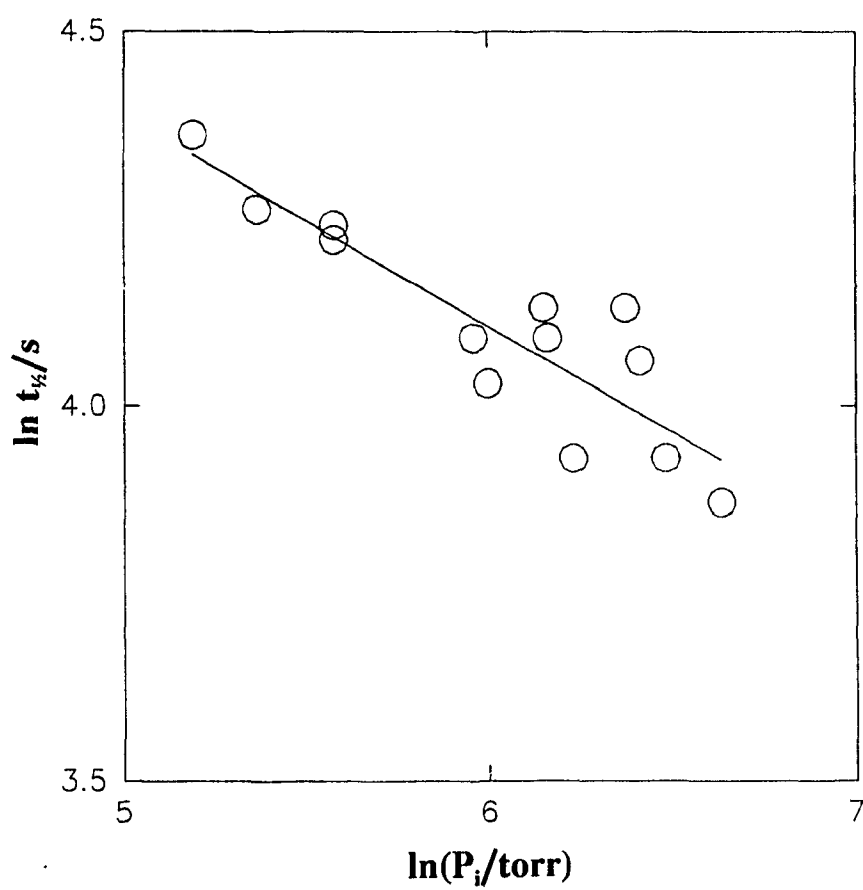


Fig. 3.1.4 Logarithmic variation of response time with initial pressure in an experiment at 773 K. The size of bulb B' for this experiment was 2 litres.

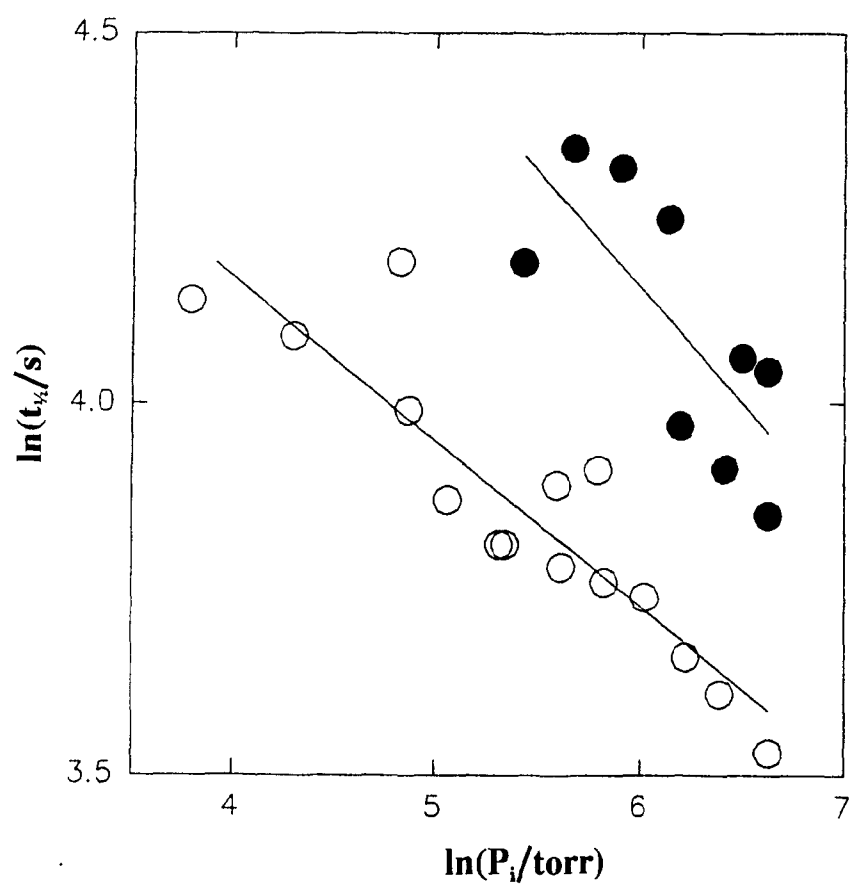


Fig. 3.1.5 Logarithmic variation of response time with initial pressure in experiments at 773 K. $\circ$ $B' = 100$ ml; $\bullet$ $B' = 2$ ml.

Table 3.1.4 Effect of P_i on $t_{1/2}$ at 823 K for P_i/P_f about 14

P_i (torr)	P_f (torr)	ΔE , theo, (mV)	ΔE_f , (mV)	t_f (s)	$t_{1/2}$ (s)
765	54.4	46.9	41.6	99.2	4.8
732	51.9	46.9	42.2	99.2	4.6
539	38.0	47.0	39.7	99.2	4.6
440	31.0	47.0	44.2	99.2	4.8
353	24.8	47.1	44.2	99.2	4.6
287	20.2	47.1	44.8	99.2	4.8
157	11.0	47.1	44.8	93.0	4.8
109	7.64	47.2	43.8	99.0	4.6
54.7	3.74	47.6	41.6	96.0	5.2

Table 3.1.5 Effect of P_i on $t_{1/2}$ at 873 K for P_i/P_f about 14

P_i (torr)	P_f (torr)	ΔE , theo, (mV)	ΔE_f , (mV)	t_f (s)	$t_{1/2}$ (s)
764	53.9	49.9	44.1	8.8	1.4
670	47.4	49.8	42.2	8.8	1.6
603	42.5	49.9	42.9	8.8	1.5
522	36.5	50.0	42.9	8.8	1.4
433	30.6	49.9	41.6	9.0	1.5
358	25.5	49.7	42.9	8.2	1.4
317	22.1	50.1	44.8	9.0	1.4
206	14.4	50.0	41.6	9.0	1.6
123	8.6	50.1	44.2	9.2	1.6
68	4.5	51.2	41.0	8.4	1.9

Table 3.1.6 Effect of P_i on $t_{1/2}$ at 923 K for P_i/P_f about 14

P_i (torr)	P_f (torr)	ΔE , theo, (mV)	ΔE_r , (mV)	t_r (s)	$t_{1/2}$ (s)
765	53.6	52.8	48.9	4.0	0.32
613	43.1	52.8	48.6	4.0	0.32
498	34.8	52.9	48.0	3.8	0.34
383	26.6	53.0	48.0	3.7	0.35
294	20.8	52.7	48.0	3.6	0.34
241	16.7	53.0	48.6	3.8	0.37
144	10.0	53.0	49.3	3.8	0.35
89	6.13	53.2	46.1	3.9	0.40

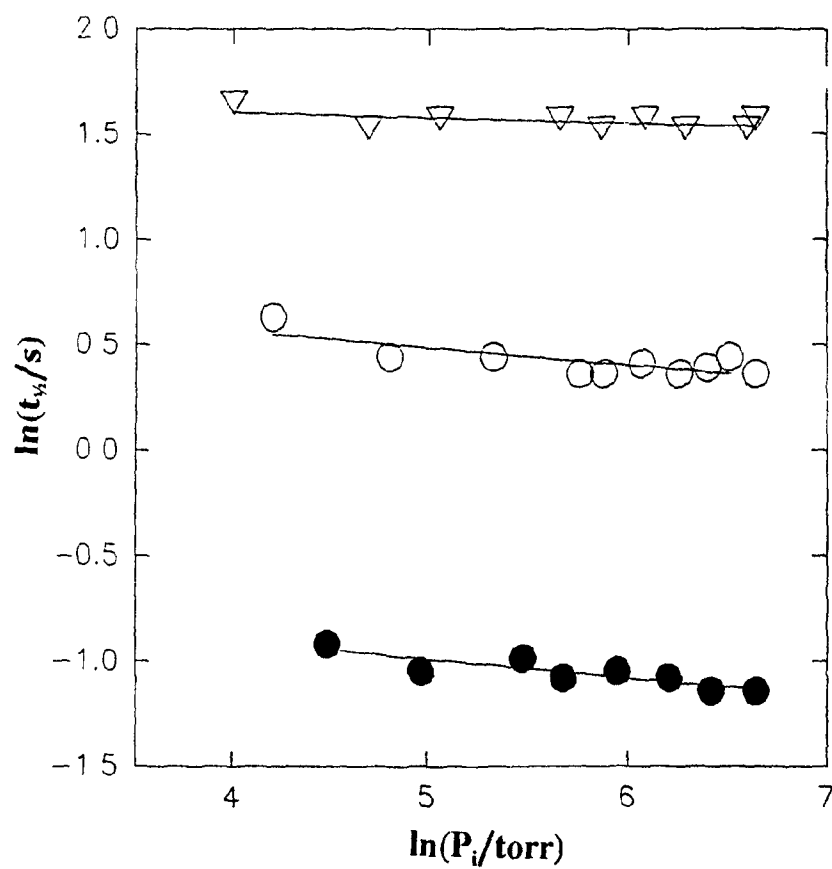


Fig. 3.1.6 Logarithmic variation of response time with initial pressure in three experiments. ∇ 823 K; $\circ$ 873 K; $\bullet$ 923 K, The ratio P_i/P_f in these experiments was 14.

Table 3.1.7 Orders or slopes of graphs in Figures 3.1.4, 3.1.5 and 3.1.6

T(K)	P_i/P_f	$d \ln t_{1/2} / d \ln P_i$
773	125	-0.28 ± 0.04
773	22	-0.22 ± 0.03
773	15	-0.31 ± 0.11
823	14	-0.03 ± 0.01
873	14	-0.08 ± 0.02
923	14	-0.09 ± 0.02

Table 3.1.8 Effect of P_i on $t_{1/2}$ at 773 K for $P_f > P_i$

P_i (torr)	P_f (torr)	ΔE , theo, (mV)	ΔE_f , (mV)	t_f (s)	$t_{1/2}$ (s)
561	752	4.89	3.5	60	36
450	742	8.32	7.0	184	30
303	740	14.9	11.3	11	28
208	737	21.0	17.0	17	21
177	733	23.6	19.0	19	22
141	732	27.5	22.0	22	21
116	730	30.6	22.5	22	22
68	731	39.5	35.0	35	18
52	731	43.9	35.0	35	19
48	730	45.4	32.5	32	22
36	729	50.1	39.5	40	20

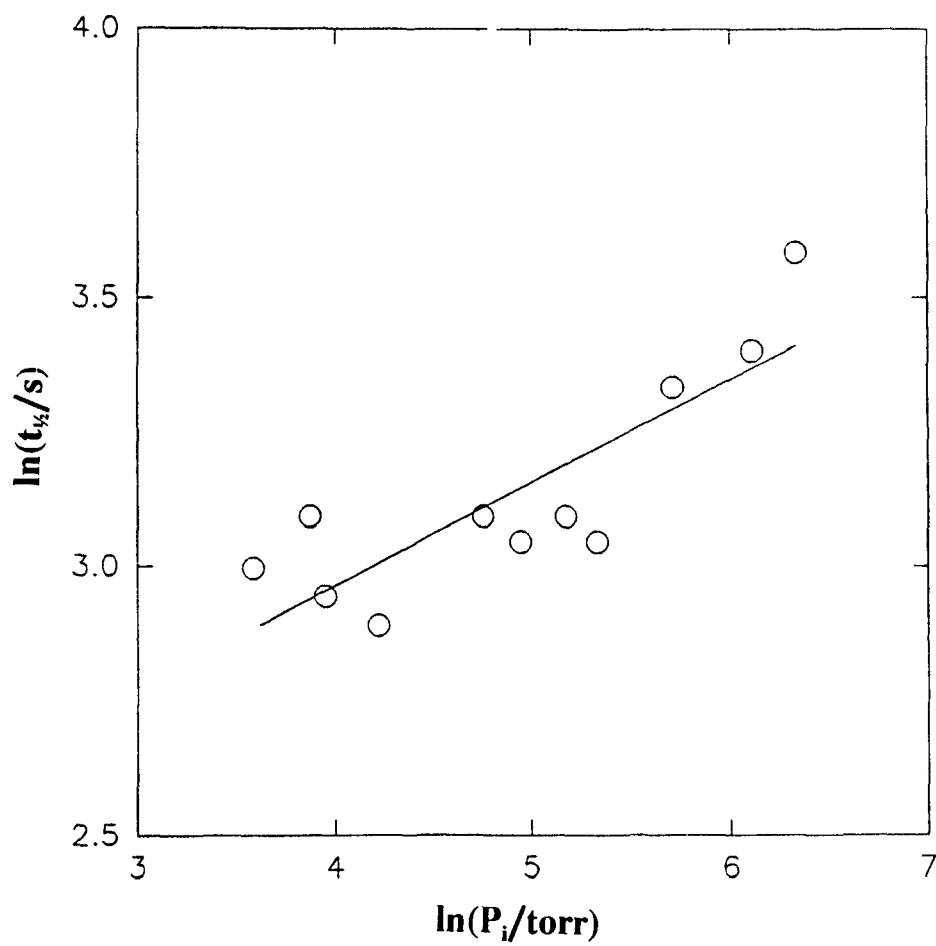


Fig. 3.1.7 Logarithmic variation of response time with initial pressure when the pressure was changed from low to high at 773 K.

values of P_i and P_f . The temperature was increased from 773 K up to 923 K as shown in Tables 3.1.9 to 3.1.11 and it was observed that the sensor responded faster with increase in temperature. Figure 3.1.8 shows Arrhenius plots for the response time as a function of inverse temperature ($1000/T$). The activation energies and the pre-exponential factors were calculated using the method of linear regression⁶⁶ and are reported in Table 3.1.12. The average value of the activation energy was $210 \pm 14 \text{ kJ mol}^{-1}$ and the pre-exponential factor was $10^{12.8 \pm 0.9} \text{ s}^{-1}$. To calculate the average value, a weight factor proportional to the inverse square of standard deviations was used.

Tables 3.1.13 to 3.1.17 show $t_{1/2}$ as a function of P_i/P_f at 773 K, 823 K, 898 K, 923 K and 948 K respectively. The ratio P_i/P_f was varied by changing the bulb size. Smaller bulb gave a higher value of P_f and a smaller P_i/P_f ratio. It was observed that $t_{1/2}$ decreased on decreasing P_i/P_f and on increasing the temperature from 773 K to 948 K. Since the value of P_i was same, the response time changed due to the change in the value of P_f . In Fig. 3.1.9, the logarithm of $t_{1/2}$ was plotted against the logarithm of P_f . Slopes were obtained using the method of linear regression and are given in Table 3.1.18. At lower temperature (773 K) the slope was about $-1/4$ decreasing slightly at higher temperatures.

3.2 Response time measurements on sensor B

The response time of the sensor to rapid changes in the pressure was measured using the same technique as for sensor A. Fig 3.2.1 shows a trace obtained on the oscilloscope of voltage at 773 K vs time. From the trace of EMF vs time

Table 3.1.9 Effect of temperature on the response time of sensor A for $P_i = 768$ torr,
 $P_f = 54$ torr

T (K)	ΔE , theo, (mV)	ΔE_r , (mV)	t_r (s)	$t_{1/2}$ (s)
773	44.1	33.9	99	30.8
778	44.7	35.2	99	30.0
783	44.9	33.9	99	30.0
788	45.0	37.8	99	23.2
793	45.3	39.7	99	15.2
798	45.7	42.9	99	14.8
803	46.0	42.2	99	13.6
808	46.3	40.3	98	10.0
813	46.6	45.4	99	8.0
818	46.8	45.8	99	7.2
823	46.8	35.2	19	6.6
833	47.8	29.4	8.5	5.8
848	48.5	35.2	8.9	3.9

Contd..

Contd. from page 64,

T (K)	ΔE , theo, (mV)	ΔE_r , (mV)	t_r (s)	$t_{1/2}$ (s)
873	49.9	42.2	8.5	2.7
898	51.6	49.3	8.8	1.7
923	53.1	48.0	8.3	1.3

Table 3.1.10 Effect of temperature on the response time of sensor A for $P_i = 753$ torr, $P_f = 53$ torr

T (K)	ΔE, theo, (mV)	ΔE_r, (mV)	t_r(s)	$t_{1/2}$(s)
773	44.3	23.7	100	78
783	45.1	32.6	100	42
793	45.2	33.9	100	31
803	45.8	39.0	50	10
813	46.5	36.5	19	4.2
823	47.1	36.2	8.8	2.4
825	47.2	32.0	8.9	3.3
844	48.4	40.3	8.4	1.6
848	48.6	37.8	8.5	1.5
875	50.3	42.2	8.2	0.80
898	51.7	45.4	3.9	0.40

Table 3.1.11 Effect of temperature on the response time of sensor A for $P_i = 765$ torr,
 $P_t = 53$ torr

T (K)	ΔE, theo, (mV)	ΔE_r, (mV)	t_r (s)	$t_{1/2}$ (s)
773	44.2	30.1	98	44
783	44.8	32.6	98	33
793	45.4	35.8	98	27
803	46.0	37.8	98	20
813	46.6	39.7	98	16
823	47.2	43.5	98	10
833	47.8	43.5	98	7.2
848	48.7	44.4	47	4.4
870	50.2	46.1	49	1.6
898	51.7	47.3	8.1	0.56
923	52.7	48.0	4.0	0.21

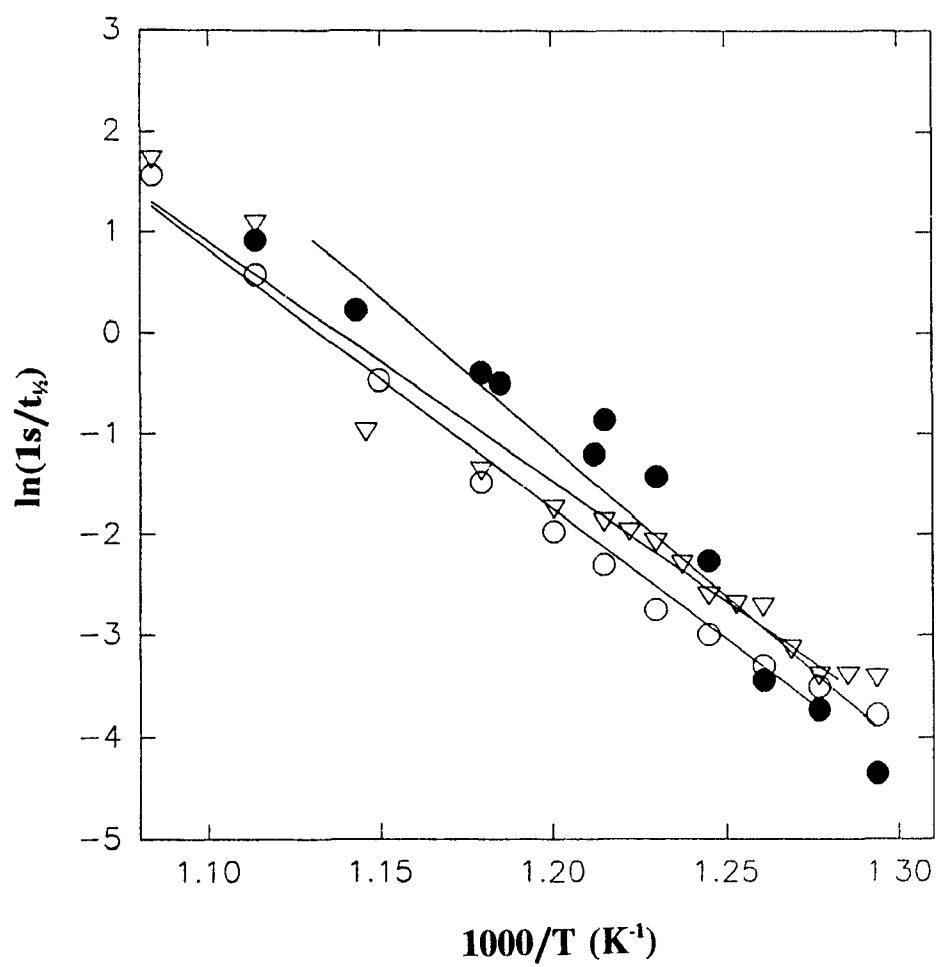


Fig. 3.1.8 Arrhenius plot of response time as a function of inverse temperature for sensor A.

Table 3.1.12 Arrhenius parameters for sensor A

Run no.	E_A kJ mol ⁻¹	Pre-exp. factor s ⁻¹
1	197 ± 11	$10^{11.7 \pm 1.7}$
2	246 ± 22	$10^{14.9 \pm 1.4}$
3	213 ± 9	$10^{12.6 \pm 0.6}$

Table 3.1.13 Effect of P_i/P_f on $t_{1/2}$ at 773 K for sensor A

P_i (torr)	P_f (torr)	P_i/P_f	ΔE , theo, (mV)	ΔE_f , (mV)	t_f (s)	$t_{1/2}$ (s)
766	5.62	136	81.8	50.4	100	59
766	9.89	77	72.4	46.4	100	54
766	16.8	46	63.6	40.2	100	50
765	25.0	31	57.0	41.8	100	36
765	33.6	23	52.0	38.2	100	34
765	40.7	19	48.8	34.9	100	37
765	44.6	17	47.3	33.9	100	37
765	49.9	15	45.5	33.4	100	31

Table 3.1.14 Effect of P_i/P_f on $t_{1/2}$ at 823 K for sensor A

P_i (torr)	P_f (torr)	P_i/P_f	ΔE , theo, (mV)	ΔE_f , (mV)	t_f (s)	$t_{1/2}$ (s)
770	5.57	138	87.4	51.4	50	33
770	9.56	80	77.6	49.9	50	29
770	16.8	46	67.8	44.8	50	26
770	25.2	31	60.6	40.8	50	25
770	33.9	23	55.4	37.2	50	23
770	50.1	15	48.4	34.1	50	20

Table 3.1.15 Effect of P_i/P_f on $t_{1/2}$ at 848 K for sensor A

P_i (torr)	P_f (torr)	P_i/P_f	ΔE , theo, (mV)	ΔE_f , (mV)	t_f , (s)	$t_{1/2}$ (s)
769	5.5	139	90.1	69.3	50	14
769	9.8	78	79.6	61.1	50	13
769	16.9	46	69.7	57.1	50	11
769	25.1	31	62.5	53.0	50	10
769	33.5	23	57.2	48.9	50	8
769	50.0	15	49.9	42.8	50	8

Table 3.1.16 Effect of P_i/P_f on $t_{1/2}$ at 923 K for sensor A

P_i (torr)	P_f (torr)	P_i/P_f	ΔE , theo, (mV)	ΔE_f , (mV)	t_f (s)	$t_{1/2}$ (s)
753	5.26	139	98.7	97.3	5.0	0.31
753	9.34	78	87.3	87.0	5.0	0.28
757	16.1	46	76.6	76.1	2.0	0.24
757	24.3	31	68.4	67.8	2.0	0.21
761	32.7	23	62.6	61.8	2.0	0.24
762	43.1	18	57.1	56.3	2.0	0.20
762	39.3	19	58.9	58.9	2.0	0.23
761	43.1	18	57.1	54.4	2.0	0.20

Table 3.1.17 Effect of P_i/P_f on $t_{1/2}$ at 948 K for sensor A

P_i (torr)	P_f (torr)	P_i/P_f	ΔE , theo, (mV)	ΔE_f , (mV)	t_f (s)	$t_{1/2}$ (s)
759	5.38	141	101	98.5	2.0	0.33
759	9.26	82	90.0	85.7	2.0	0.29
759	16.4	46	78.2	76.8	2.0	0.24
759	24.4	31	70.2	68.3	2.0	0.19
761	32.4	23	64.5	65.0	2.0	0.19
763	43.4	18	58.4	58.5	2.0	0.28
763	39.4	19	60.5	61.8	2.0	0.28
759	49.2	15	55.9	55.2	2.0	0.18

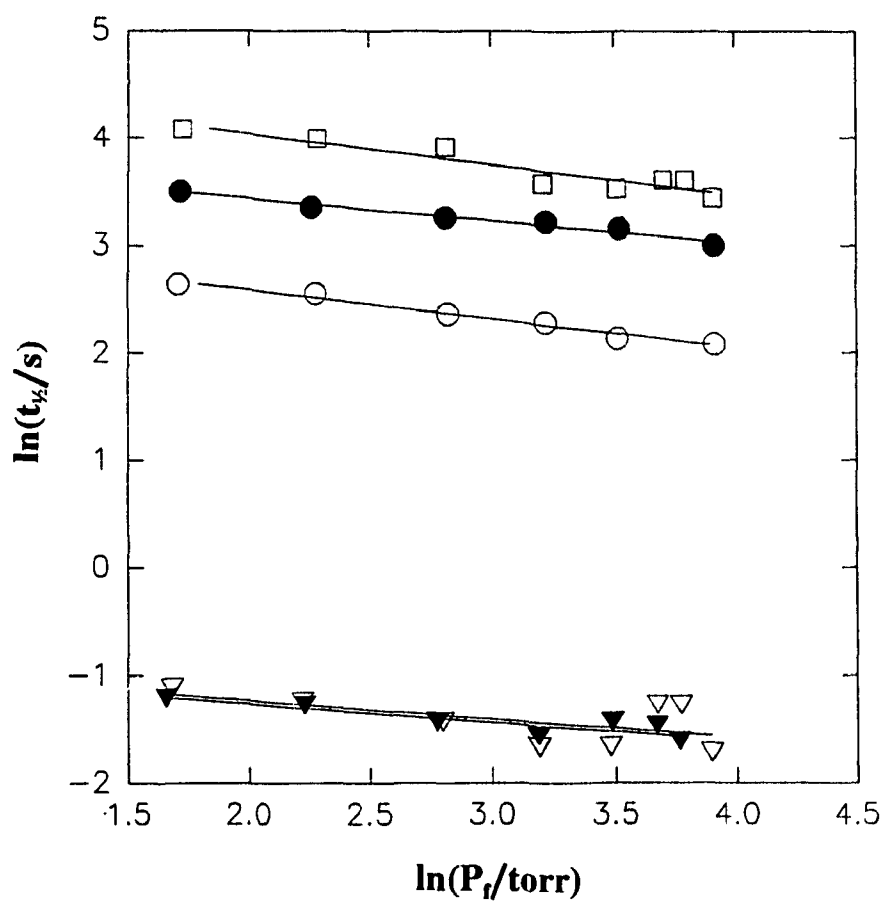


Figure 3.1.9 Logarithmic variation of response time with final pressure when the ratio P_i/P_f was changed on changing the bulb size. $\square$ 773 K; $\bullet$ 823 K; $\circ$ 848 K; $\blacktriangledown$ 923 K; $\triangledown$ 948 K. P_i was 760 torr for these experiments.

Table 3.1.18 Orders or slopes of lines in Figure 3.1.9.

T(K)	P _i (torr)	dln t _{1/2} /dln P _f
773	765	-0.29 ± 0.04
823	770	-0.21 ± 0.02
848	769	-0.27 ± 0.02
923	757	-0.17 ± 0.03
948	760	-0.17 ± 0.10

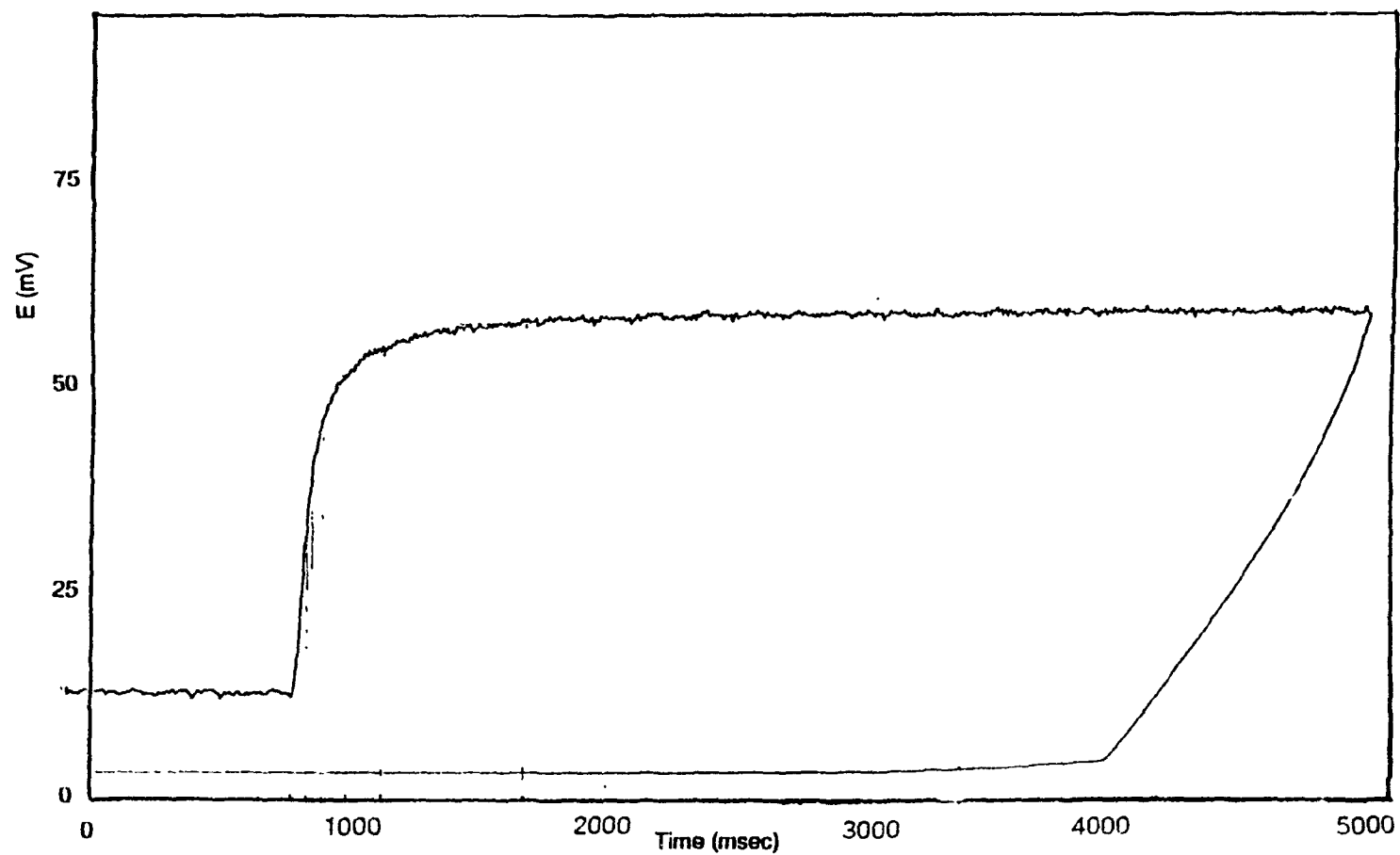


Fig 3.2.1 A trace of EMF vs time at 773 K obtained on the oscilloscope for sensor B.

$t_{1/2}$ and $t_{0.63}$ were calculated. The response time, $t_{1/2}$, has been defined earlier and $t_{0.63}$ is the time required for the sensor voltage to change by 63 % of its theoretical Nernstian value.³⁰ It can be seen that for the freshly prepared sensor B, the response was faster than that of sensor A. At 773 K, $t_{1/2}$ and $t_{0.63}$ were observed to be 63 and 90 ms, respectively. The value of $t_{1/2}$ for sensor B was two orders of magnitude smaller than that of sensor A.

The response time of the sensor was studied as a function of the initial pressure from 773 torr to 66 torr at 623 K, 673 K, 723 K, 773 K, 823 K and 860 K, as shown in Tables 3.2.1 to 3.2.6. The response time was observed to be less dependent on the initial pressure at all the above temperatures as shown in Fig.3.2.2 and Table 3.2.7. It is seen that the orders were positive and very small.

Response times were studied as a function of temperature and were found to decrease with increase in temperature. Table 3.2.8 shows the effect of temperature and aging on $t_{0.63}$. The value of $t_{0.63}$ increased considerably due to aging. In Fig 3.2.3 $\ln(1/t_{0.63})$ was plotted against $1/T$ for the four sets of experiments done during different time periods of the sensor B. The activation energies obtained from the slopes and the pre-exponential factors obtained from the intercepts are reported in Table 3.2.9. It was observed that the activation energies and the pre-exponential factors were a little different for different ages of the sensor but no trend was found.

Table 3.2.1 Dependence of response time on initial pressure at 623 K for sensor B

P_i torr	P_f torr	ΔE , theo, mV	ΔE_f , (mV)	t_r (s)	$t_{1/2}$ s
755	49.3	36.6	36.5	198	25
614	39.8	36.7	35.8	198	27
511	32.9	36.8	38.3	200	27
452	30.1	36.4	37.1	192	27
337	22.0	36.6	36.5	200	27
231	15.0	36.7	39.7	200	25
154	9.91	36.8	37.8	200	26
72.9	4.78	36.6	38.4	200	25

Table 3.2.2 Dependence of response time on the initial pressure at 673 K

P_i torr	P_f torr	ΔE , theo, (mV)	ΔE_f , (mV)	t_f (s)	$t_{1/2}$ (s)
772	50.7	39.5	30.1	100	16.4
621	40.4	39.6	27.5	100	16.4
513	33.5	39.6	28.8	98	17.2
394	25.8	39.5	28.8	100	16.8
246	16.3	39.4	29.4	100	16
175	11.6	39.4	30.1	100	14.8
113	7.28	39.7	30.1	100	14.4

Table 3.2.3 Dependence of response time on the initial pressure at 723 K for sensor B

P_i torr	P_f torr	ΔE , theo, (mV)	ΔE_r , (mV)	t_r (s)	$t_{1/2}$ (s)
773	50.0	42.7	40.3	48	2.0
607	38.9	42.8	38.4	48	1.8
483	30.8	42.9	40.3	48	1.8
354	22.6	42.8	39.7	48	1.8
222	14.1	42.9	40.3	48	1.6
119	7.43	43.2	40.3	48	1.6
64.0	4.24	42.3	38.4	49	1.6

Table 3.2.4 Dependence of response time on the initial pressure at 773 K for sensor B

P_i torr	P_f torr	ΔE , theo, mV	ΔE_f , (mV)	t_f (s)	$t_{1/2}$ (s)
773	49.6	45.7	43.5	10.0	0.36
648	41.3	45.8	40.3	4.0	0.36
507	32.5	45.7	41.0	4.0	0.34
395	25.4	45.7	39.7	4.0	0.34
272	17.6	45.6	41.0	3.9	0.32
77.3	5.19	45.0	39.7	4.0	0.24

Table 3.2.5 Dependence of response time on the initial pressure at 823 K for sensor B

$P_i(\text{torr})$	$P_f(\text{torr})$	$\Delta E, \text{theo, (mV)}$	$\Delta E_r, (\text{mV})$	$t_r (\text{s})$	$t_h (\text{s})$
762	48.2	49.0	48.0	3.9	0.16
577	36.2	49.1	49.1	4.0	0.16
479	30.2	49.0	49.2	4.0	0.14
386	24.3	49.0	49.3	4.0	0.14
274	17.5	48.8	48.6	3.9	0.14
193	12.3	48.7	48.6	3.7	0.14
119	7.54	48.9	48.6	3.9	0.14
66.7	4.29	48.7	47.3	3.9	0.16

Table 3.2.6 Dependence of response time on initial pressure at 860 K for sensor B

P_i (torr)	P_R (torr)	ΔE , theo, (mV)	ΔE_r , (mV)	t_r (s)	$t_{1/2}$ (s)
764	48.5	51.1	51.1	4.0	0.06
619	39.1	51.2	51.2	3.7	0.05
464	29.0	51.3	51.2	4.0	0.06
344	21.7	51.2	51.2	3.8	0.05
264	16.8	51.0	52.4	4.0	0.05
140	9.03	50.8	52.5	3.9	0.05
66.0	4.16	51.2	51.2	3.8	0.05

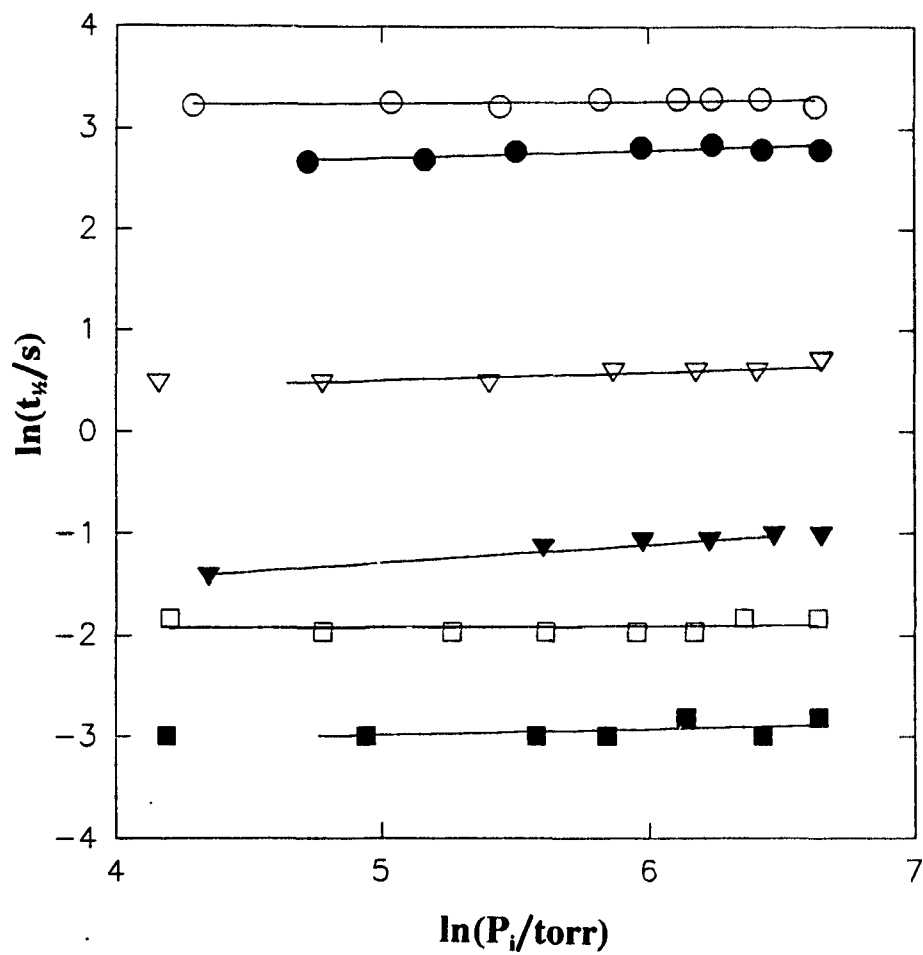


Fig. 3.2.2 Logarithmic variation of response time with initial pressure of the experiment for sensor B, ○ 623 K; ● 673 K; ▽ 723 K; ▼ 773 K; □ 823 K; ■ 860 K.

Table 3.2.7 Orders of graphs in Figure 3.2.2

T(K)	$\text{dln } t_{1/2}/\text{dln } P_i$
623	0.022 ± 0.017
673	0.080 ± 0.021
723	0.083 ± 0.021
773	0.179 ± 0.017
823	0.009 ± 0.033
860	0.058 ± 0.038

Table 3.2.8 Response times of sensor B (freshly prepared, after 3 weeks, 3 months and 6 months of aging)

T/K	$t_{0.63}$ s	$t_{0.63}$ s	$t_{0.63}$ s	$t_{0.63}$ s
	2 weeks	3 weeks	3 months	6 months
860		0.09		
823	0.08	0.18	0.54	0.9
773	0.09	0.68	1.5	2.6
723	0.46	3.6	7.4	18
673	3.75	44.0	59.0	144
623	38.0		79.0	492

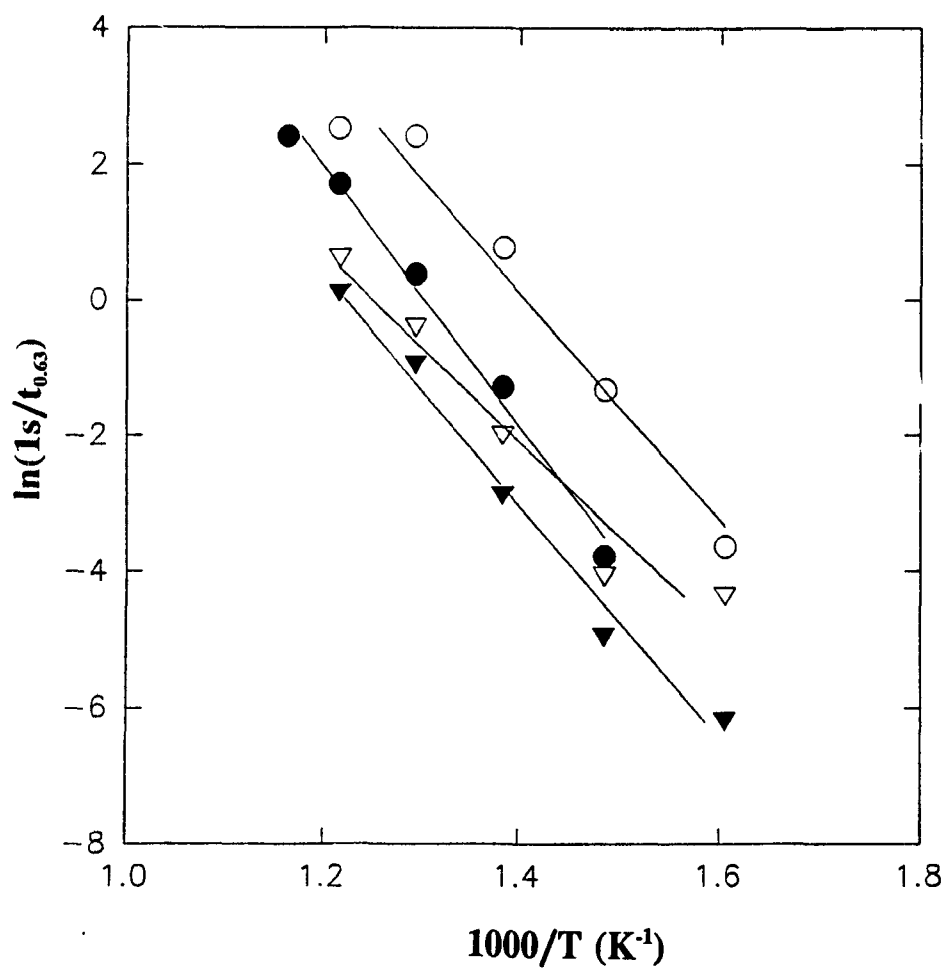


Fig. 3.2.3 Arrhenius plot of $\ln(1/t_{0.63})$ as a function of inverse temperature for sensor B,
 ○ 2 weeks; ● 3 weeks; ▽ 3 months; ▼ 6 months of aging

Table 3.2.9 Arrhenius parameters for sensor B

Age of sensor	E_A kJ mol ⁻¹	A s ⁻¹
2 weeks	139 ± 15	$10^{10.2 \pm 1.1}$
3 weeks	159 ± 9	$10^{10.8 \pm 0.7}$
3 months	115 ± 16	$10^{7.5 \pm 1.2}$
6 months	141 ± 10	$10^{9.0 \pm 0.7}$

3.3 Impedance Measurements on Sensor B

3.3.1. Description of the Tables of Measurements

Fig. 3.3.1 shows a typical Lissajous figure obtained on the X-Y recorder with sensor B. From the range of the x and y axes and the dimensions of the ellipse, the real and imaginary components of the impedance were calculated using eqs. 1.16 and 1.17 given in the Introduction.

For the frequencies above 1 Hz, the amplitude ratio B/A (dB) and the phase shift, ϕ (deg) were used to calculate the real and imaginary components of the impedance using eqs. 1.16 and 1.17 given in the Introduction.

Tables 5.1 to 5.6 in the Appendix give the amplitude ratio, the phase shift obtained on the gain phase meter for frequencies of 1 Hz to 1 MHz, and the real and imaginary parts of the impedance at 773 K, 673 K, 723 K, 623 K, 823 K and 860 K.

Tables 5.7 to 5.10 show the components of the impedance at 823 K at four different pressures of 760 torr, 316 torr, 269 torr and 114 torr on the inside of the sensor.

Tables 5.11 to 5.13 give the real and imaginary components of the impedance at 673 K when the pressure on the inside of the sensor was 760 torr, 370 torr and 137 torr, respectively.

Tables 5.14 to 5.16 show the components of the impedance obtained from the voltage amplitude ratio and phase shift at 723 K at pressures of 760, 510 and 290 torr

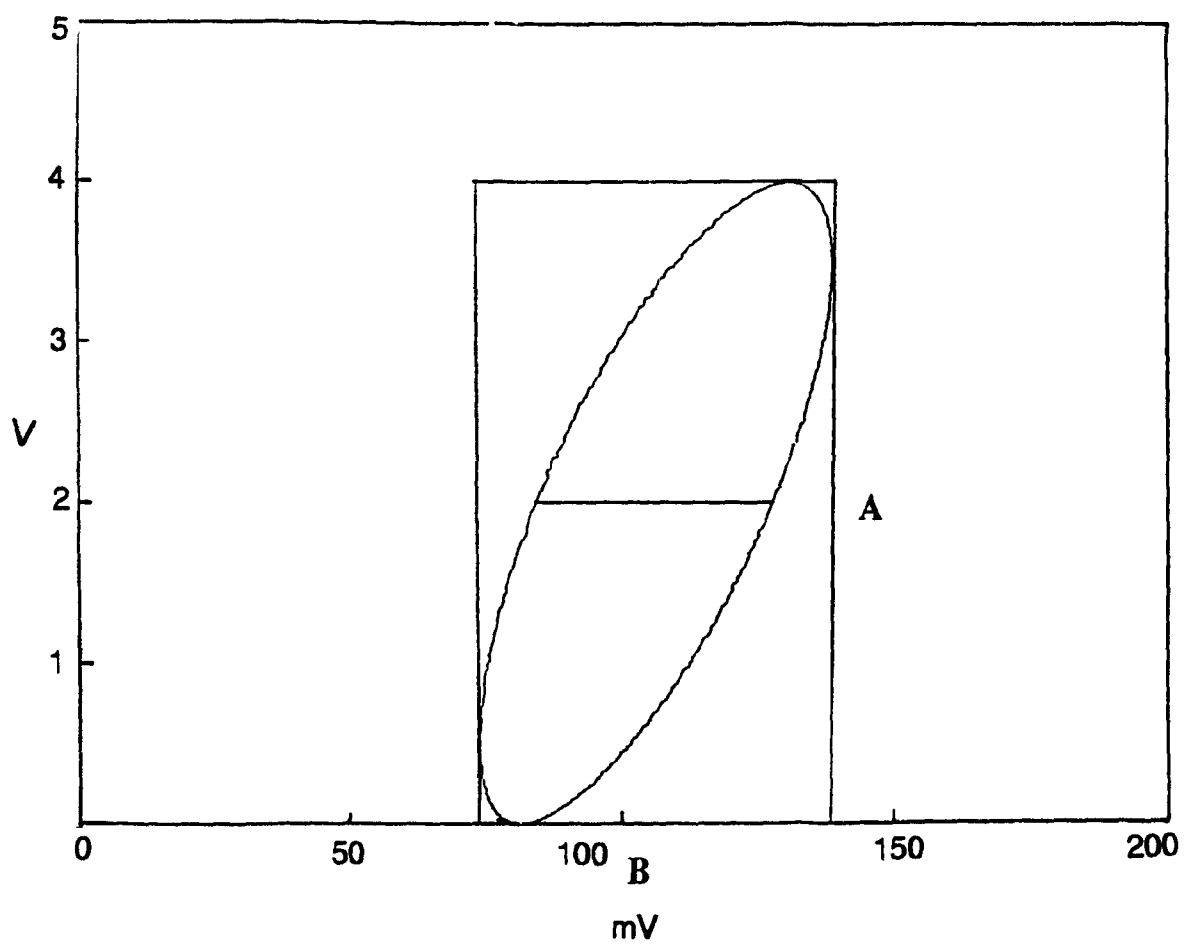


Fig. 3.3.1. A typical Lissajous figure obtained for sensor B at 773 K at a frequency of 0.09 Hz. $A = 4028 \text{ mV}$ and $B = 64.8 \text{ mV}$.

respectively.

Tables 5.17 to 5.20 give the real and imaginary parts of the impedance at 773 K when the pressures on the inside of the sensor were 760 torr, 441 torr, 248 torr and 132 torr, respectively.

Tables 5.21 to 5.24 show the effect of pressure at 823 K. The pressures on the inside of the sensor were 760 torr, 529 torr, 332 torr and 201 torr, respectively.

Tables 5.25 to 5.27 give the components of the impedance at 855 K when the pressures were 760 torr, 436 torr and 180 torr, respectively.

The measurements shown in Tables 5.1 to 5.27 were made without the high impedance interface in series with the gain phase meter or oscilloscope. Due to this, for a sensor resistance higher than 10 k Ω , the relative error was more than 1%.

Tables 5.28 to 5.32 show the impedance of the sensor from 823 K to 623 K for the measurements made on the XY recorder and the gain phase meter. Table 5.33 shows the components of the impedance obtained on the dummy sensor. The high impedance interface was used for these experiments.

To obtain an impedance diagram, the negative of the imaginary component of the impedance, $-Z''$ was plotted against the real component Z' for each excitation frequency. Fig 3.3.2 shows the impedance diagram for the dummy cell which consisted of a parallel combination of a carbon resistor (500 k Ω) and capacitor (1×10^{-6} F). An almost perfect semicircle was obtained. Fig.3.3.3 shows typical complex impedance diagrams obtained at 823 K and 860 K with sensor B. Usually one semicircle was observed at a particular temperature, but in some cases a very small semicircle was obtained at very high

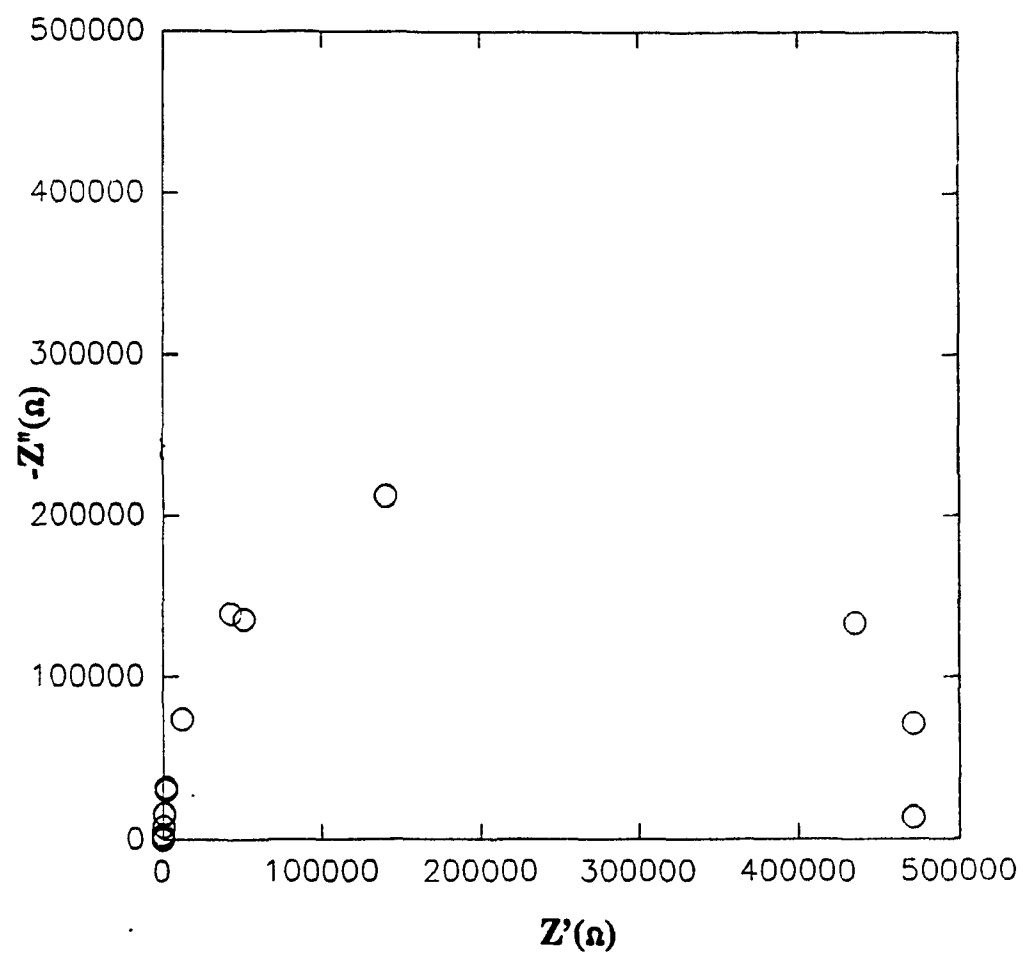


Fig.3.3.2. Complex impedance diagram for a dummy sensor with $R = 500 \text{ k}\Omega$ and $C = 1 \text{ }\mu\text{F}$.

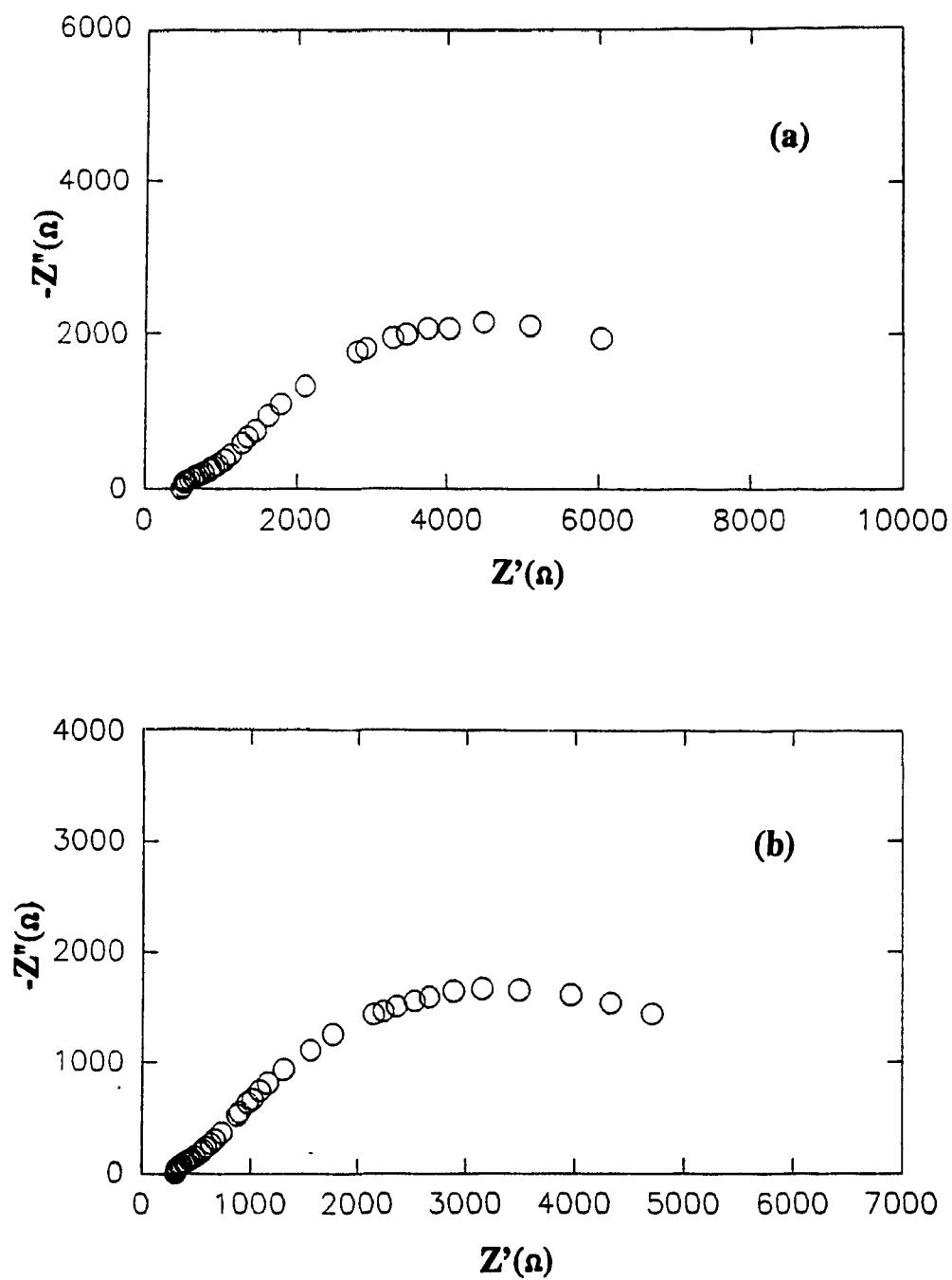


Fig. 3.3.3. Typical impedance diagrams obtained at 823 K (a) and 860 K (b). Tables 5.5 and 5.6 give the values of the real and imaginary components.

frequencies and lower temperatures. Fig.3.3.4 shows the small semicircle obtained at high frequencies at 673 K. The semicircle obtained at lower frequency was depressed (its centre was below the horizontal axis). On extrapolation, this semicircle intersected the real axis at two points, R_1 (right or lower frequency side) and R_2 (left or higher frequency side), where R_1 is the total dc resistance and R_2 is the small resistance in series. The difference $R_2 - R_1$ gives the resistance due to the larger series resistance, R_i . The parameters were obtained by fitting the following equation to the impedance diagrams using nonlinear least squares.⁶⁷

$$Z'' = [r^2 - (Z' - a)^2]^{1/2} + b \quad 3.3.1$$

This equation is illustrated in Fig. 3.3.5. In this equation, r is the radius of the semicircle in units of ohms and a and b are the horizontal and vertical coordinates, respectively, of the centre of the semicircle. So the component resistance, R_i , is

$$R_i = 2(r^2 - b^2)^{1/2} \quad 3.3.2$$

and the angle of depression, α is

$$\alpha = \sin^{-1} \frac{b}{r} \quad 3.3.3$$

The frequency corresponding to the top of the semicircle is $f_{\max}$, so that $R_i C_i 2\pi f_{\max} = 1$ for a perfect semicircle where C_i is the capacitance of this series component. The RC time constant, τ , was obtained by the equation,

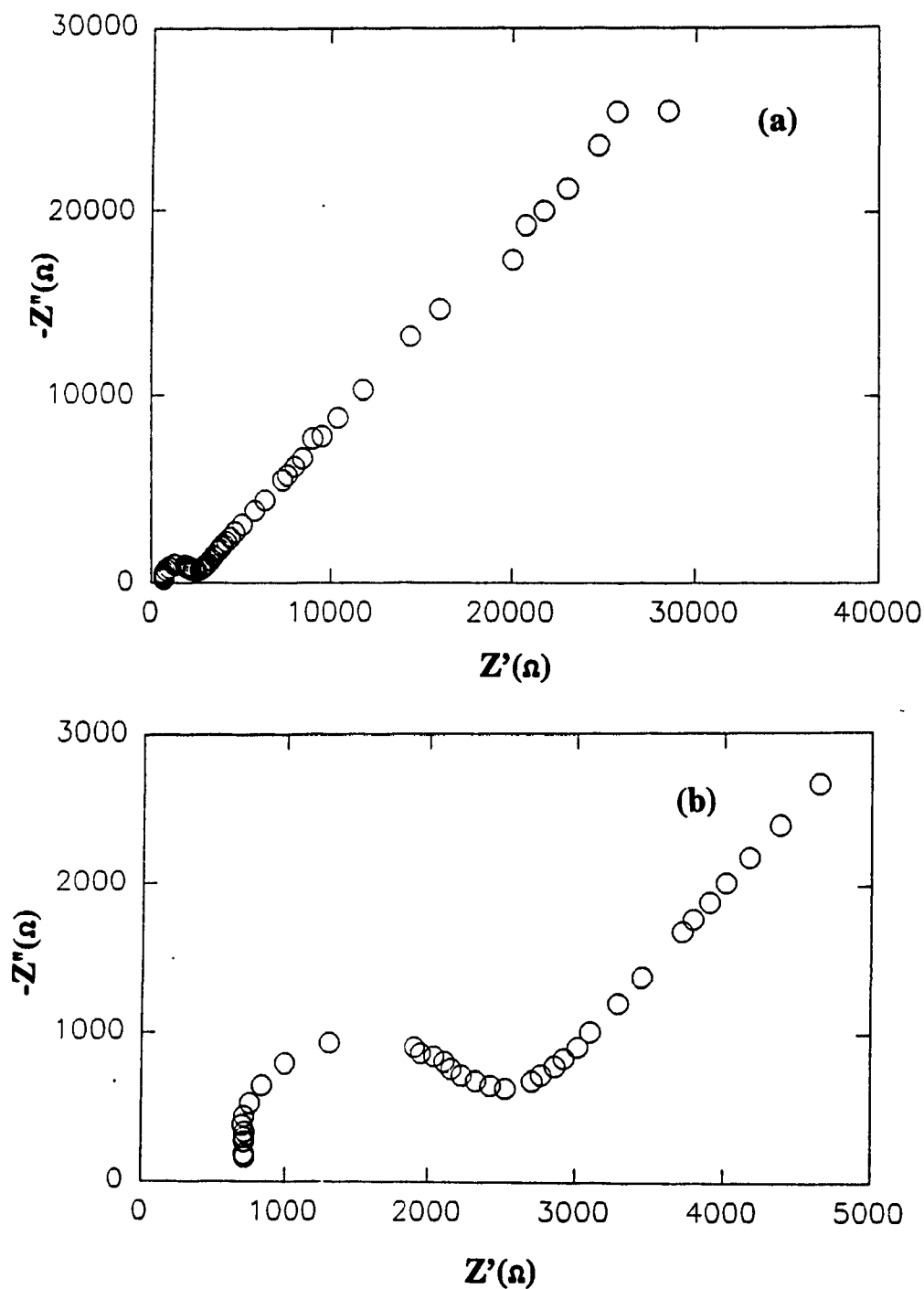


Fig.3.3.4. Complex impedance diagram for sensor B at 673 K over a frequency range from 4 Hz to 2 MHz; the data is in Table 5.2 (a) Impedance diagram from a frequency of 4 Hz to 2 MHz; (b) Part of (a) obtained at high frequency

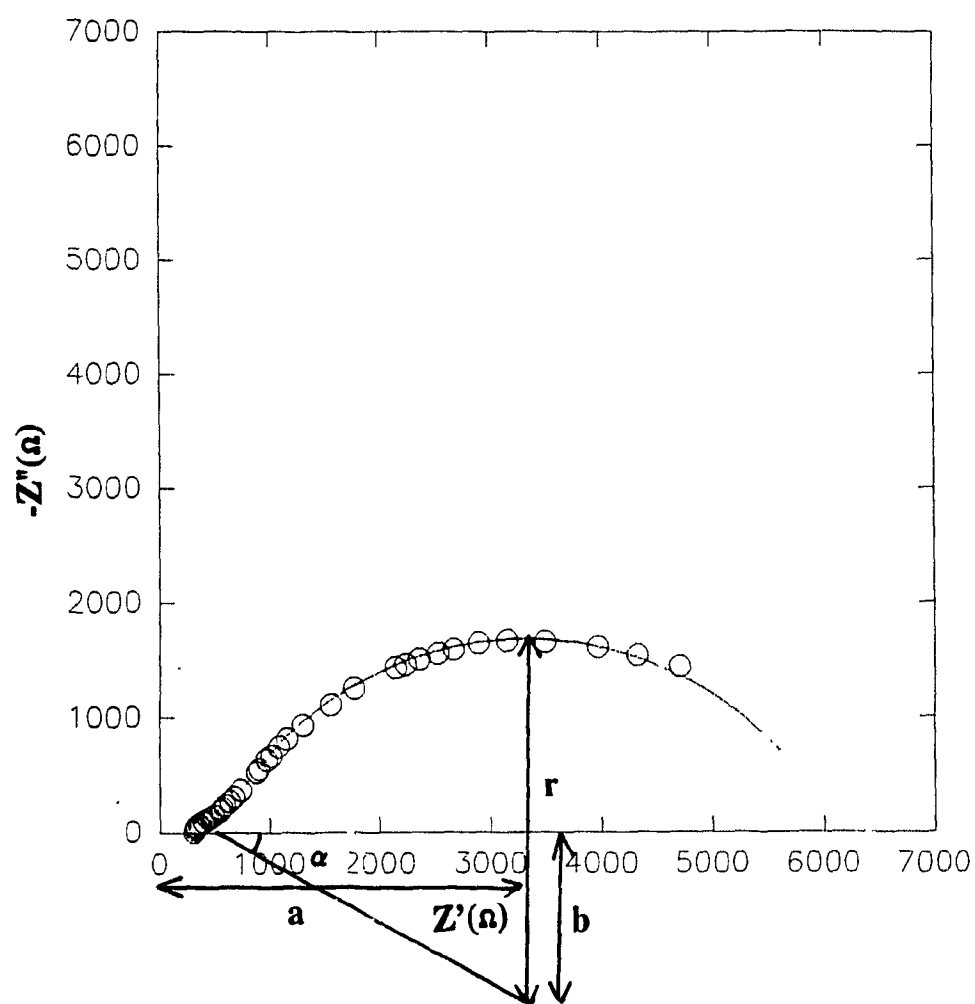


Fig 3.3.5 Calculation of impedance parameters

$$\tau = (2\pi f_{\max})^{-1} \quad 3.3.4$$

assuming that the system was approximated by a parallel RC circuit. Then the electrode capacitance was,

$$C_i = \frac{\tau}{R_i} \quad 3.3.5$$

From the impedance diagrams, it was observed that the values of resistance and the RC time constant decreased with a rise in temperature and increased due to aging.

By fitting eq.3.3.1 to the impedance plot of the dummy sensor, the values of r , a and b were calculated. The value of R was obtained to be $475 \pm 1 \text{ k}\Omega$ which is in good agreement with the real value of $499 \pm 5 \text{ k}\Omega$. The capacitance of the dummy sensor was $1 \text{ }\mu\text{F}$. So the value of $f_{\max}$ comes out to be 2 Hz . The angle of depression was 0.42 ± 0.79 degrees which is too small to be significant. Since the impedance arc obtained for the dummy cell was not depressed, so the depression observed with the sensor came from the sensor itself and was not due to the measuring equipment. A similar experiment was done by Wang and Nowick.⁴⁵

The larger series resistance was measured as a function of the internal pressure of air at 773 K , 823 K and 860 K as shown in Table 3.3.1. In Figure 3.3.5, the logarithm of R_i was plotted against the logarithm of P at 773 K , 823 K and 860 K . The slopes were obtained using the method of linear regression⁶⁶ and were found to be -0.19 ± 0.07 , -0.19 ± 0.07 and 0.07 ± 0.14 respectively.

Table 3.3.1 Effect of pressure on the resistance, capacitance and the angle of depression from the larger semicircle at some temperatures

P	R _i	f _{max}	R _i C _i	C _i	α
torr	k ohms	Hz	s	μ F	deg
T=773 K					
760	148 ± 8	0.25	0.53	4	28 ± 2
441	181 ± 5	0.2	0.8	4	32 ± 1
248	212 ± 9	0.2	0.8	4	37 ± 2
132	206 ± 18	0.2	0.8	4	30 ± 3
T=823 K					
760	41 ± 1	0.6	0.3	6	32 ± 1
529	46 ± 1	0.4	0.4	9	32 ± 1
332	54 ± 1	0.2	0.8	15	35 ± 1
201	52 ± 3	0.4	0.4	8	33 ± 3
T=855 K					
760	14.4 ± 0.6	1.5	0.11	8	36 ± 2
436	11.4 ± 0.4	2	0.08	7	33 ± 1
180	12.6 ± 0.6	1.5	0.11	8	36 ± 2

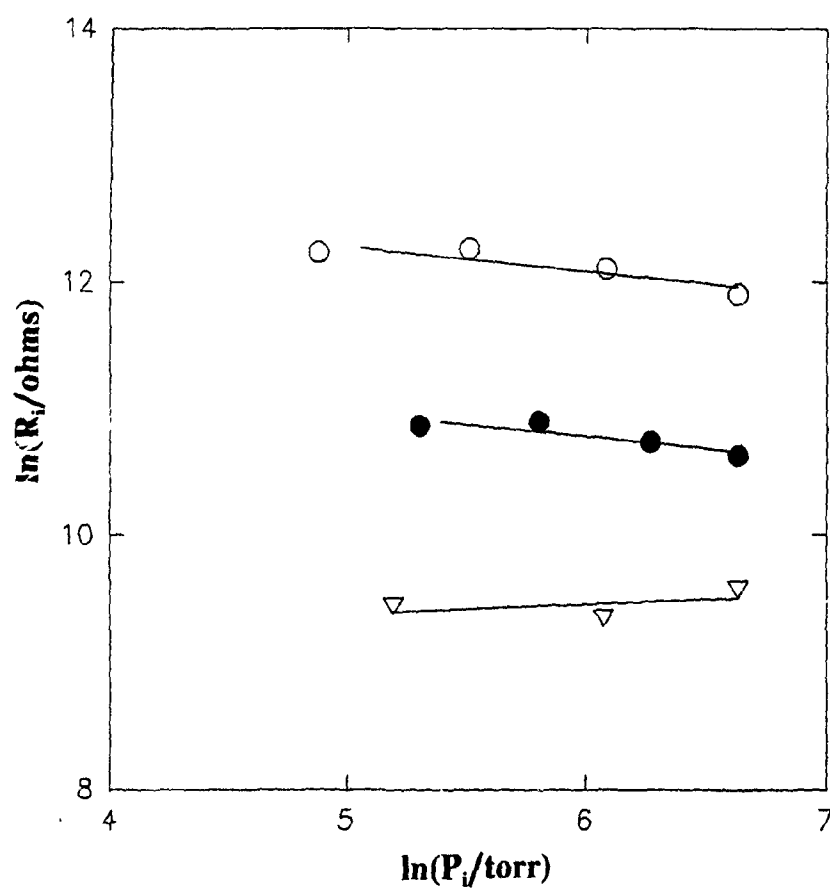


Fig.3.3.6 Logarithmic variation of the larger series resistance with the partial pressure of oxygen in the sensor. $\circ$ 773 K; $\bullet$ 823 K; ∇ 860 K.

The smaller series resistance, R_s , was obtained from the impedance diagrams by extrapolation of the high frequency arc to the real axis. The value of R_s was observed as a function of the partial pressure of oxygen at 673 K. This resistance, did not show any dependence on pressure as shown in Table 3.3.2.

Table 3.3.3 shows the values of R_i , $f_{\max}$, $R_i C_i$, α , $t_{0.63}$ (obtained from the vacuum technique) and C_i at 623 K, 673 K, 723 K, 773 K and 823 K. The data are in Tables 5.28 to 5.32 in the Appendix. These experiments were performed over the frequency range from 0.001 Hz to 100 kHz. It can be seen that this resistance decreased with rise in temperature but the capacitance and the angle of depression stayed the same. A similarity was observed between $R_i C_i$ and $t_{0.63}$. In Fig 3.3.6, the logarithm of R_i was plotted against $1/T(K)$ in the form of an Arrhenius plot. The energy of activation obtained from the slope was $119 \pm 17 \text{ kJ mol}^{-1}$ and the pre-exponential factor was $10^{-2.6 \pm 1.2}$ ohms.

Table 3.3.4 shows the value of R_s at some temperatures. The logarithm of R_s was plotted against $1/T(K)$ in the form of an Arrhenius plot in fig. 3.3.7. The activation energy obtained from the slope was $80 \pm 17 \text{ kJ mol}^{-1}$ and the pre-exponential factor was $10^{-2.6 \pm 1.2}$ ohms.

The resistance R_i increased considerably with aging. Table 3.3.5 shows the value of R_i at 823 K at different ages of the sensor. It is seen that in a period of 12 weeks, R_i changed by a factor of 6.

Table 3.3.2 Effect of the pressure on the smaller series resistance and capacitance at 673**K**

P (torr)	R_s (ohms)	C_s x 10⁻¹⁰ F
760	2900	2.7
370	2850	2.8
137	2850	2.8

Table 3.3.3 The values of interfacial resistance, capacitance, time constant and the angle of depression at some temperatures.

T (K)	$f_{\max}$	$R_i C_i$	$t_{0.63}$	R_i	α	C_i
		s	s	M ohms	deg	μF
623*	-	-	79	21.95 ± 0.18	30 ± 1	-
673	0.0025	63	59	4.40 ± 0.03	31 ± 0.4	12
723*	-	-	7.4	2.1 ± 0.5	36 ± 1	-
773	0.03	5.3	1.5	0.55 ± 0.01	35 ± 1	10
823	0.2	0.6	0.54	$0.052 \pm .001$	32 ± 1	12

* The data were not sufficient to get the point at the top of the semicircle.

Table 3.3.4 Effect of temperature on the value of R_b and C_b

T (K)	R_b ohms	$C_b \times 10^{-10} \text{ F}$
623	12500	2.5
673	2800	1.1
723	1700	1.0
773	1400	1.3
823	160	11

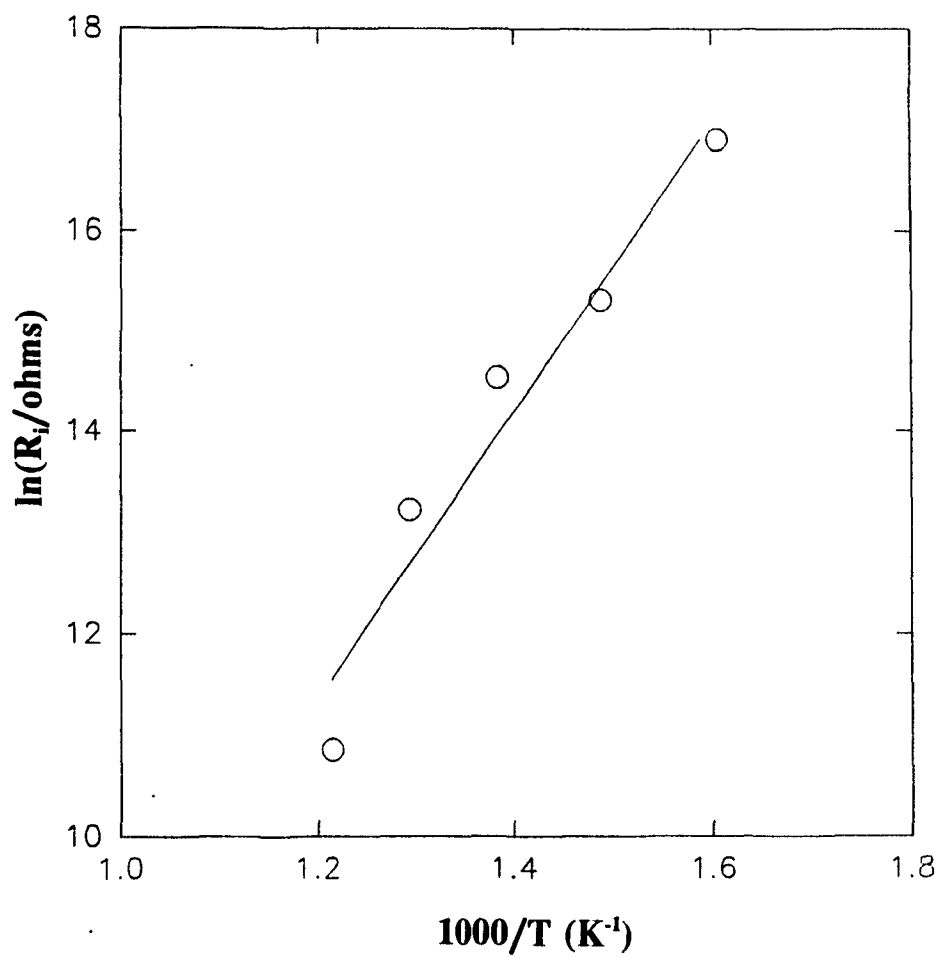


Fig. 3.3.6 Arrhenius plot of the larger series resistance, R_i as a function of inverse temperature

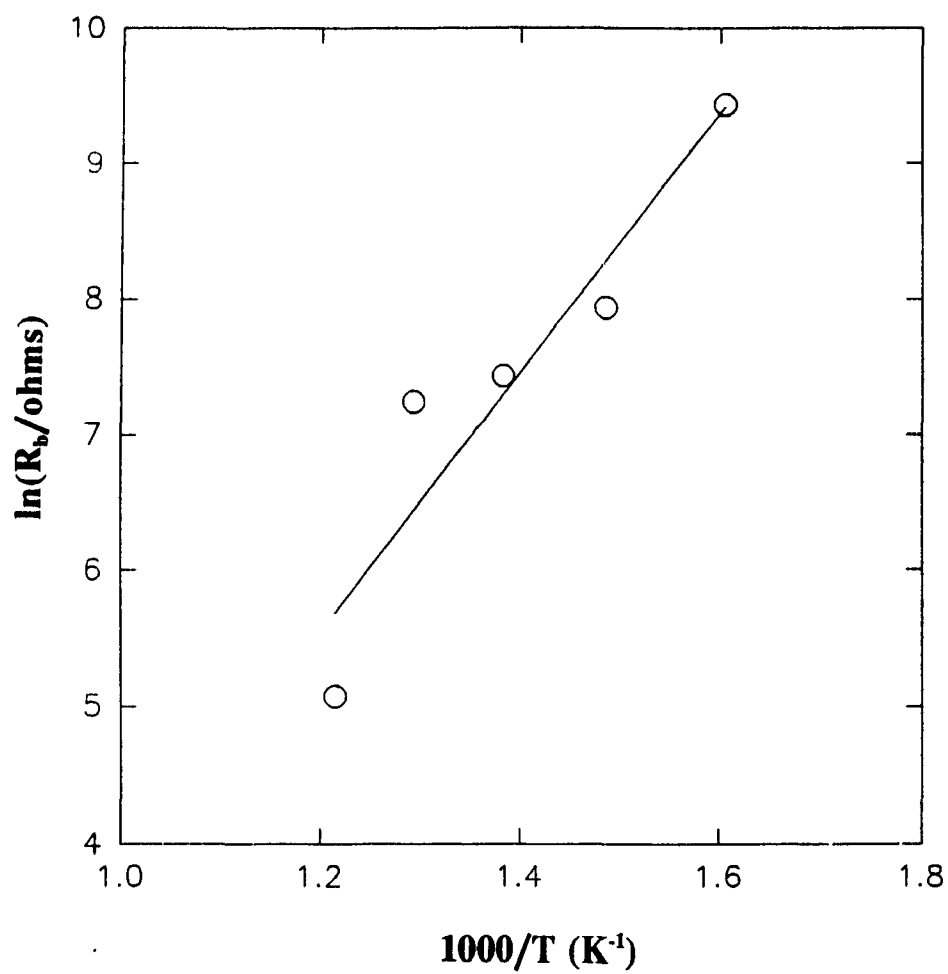


Fig. 3.3.7 Arrhenius plot of the smaller series resistance, R_s , as a function of inverse temperature.

Table 3.3.5 Effect of aging on R_i at 823 K.

Age of the sensor	R_i (kΩ)
10 days	8.5 ± 0.7
15 days	29.2 ± 0.5
3 weeks	41.1 ± 1.1
12 weeks	51.8 ± 0.8

3.4 Results from the SEM for sensor A

Fig 3.4.1 shows the scanning electron micrographs of the platinum paste on the inside of the sensor A. In these figures, two magnifications (X1000 and X2400) can be seen. It was observed that the structure was very porous. From these micrographs, the grain size was measured with a ruler. The grain size varied from 0.5 microns to 8 microns. The average grain size was 3.5 ± 1.5 microns. The pore size varied from 1.2 microns to 15 microns.

Fig 3.4.2 shows the scanning electron micrographs of a piece of platinum paste which had been directly in contact with the surface of the zirconia on the outside of the sensor. The broken surfaces in the picture were the points of contact between the platinum paste and zirconia. The size of these contacts was measured to be 0.4 microns to 2 microns with a mean value of 0.91 ± 0.38 microns. The distances between the points of contact were measured to be from 5 microns to 10 microns.

Fig 3.4.3 shows the scanning electron micrographs at a magnification of X100 of the platinum paste on the outside of the sensor A. It can be seen that the paste is not distributed homogeneously and forms small patches.

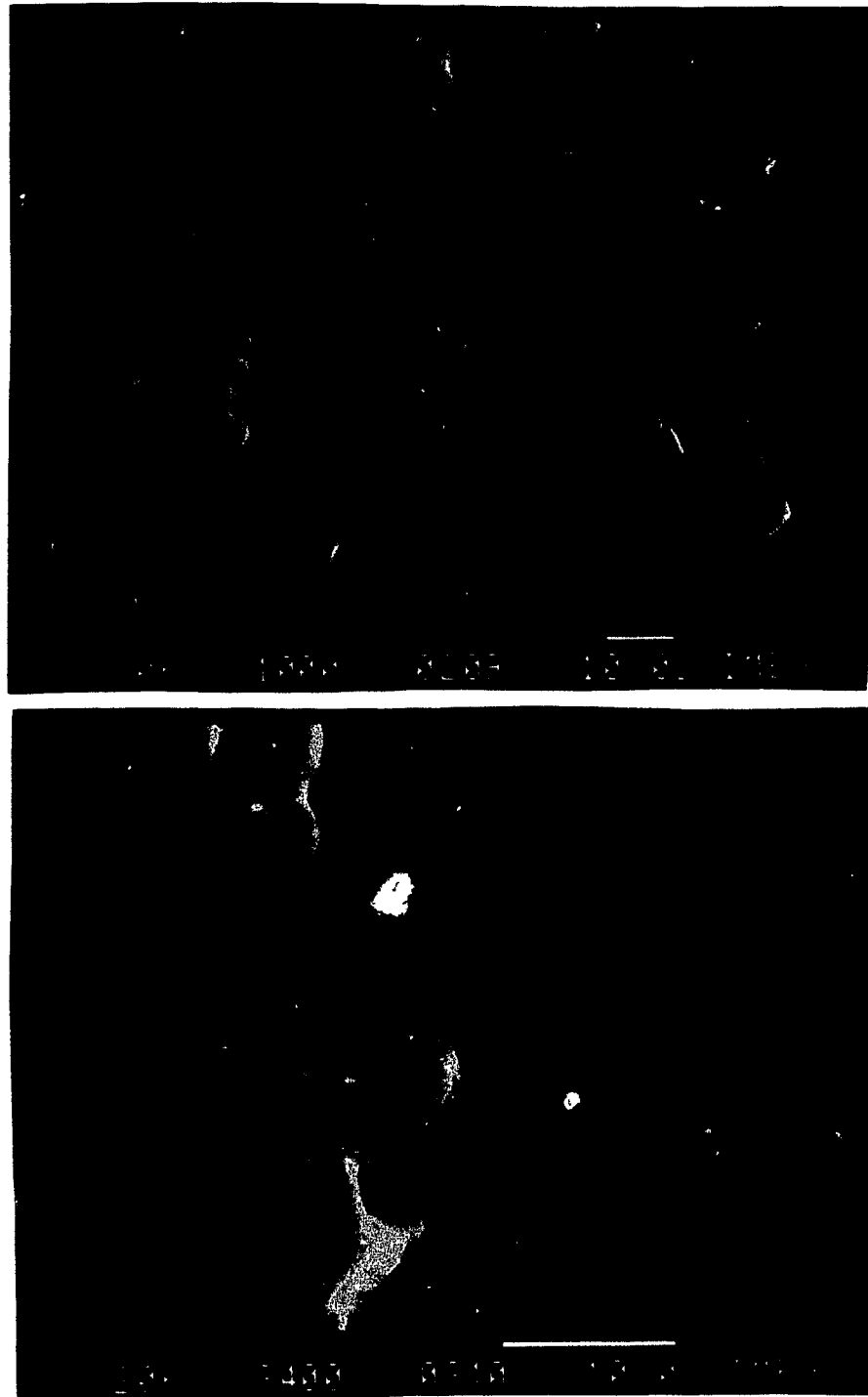


Fig 3.4.1 Scanning electron micrographs of the platinum paste on the inside of the sensor

A. (a) a magnification of X1000 **(b)** magnification of X2400.

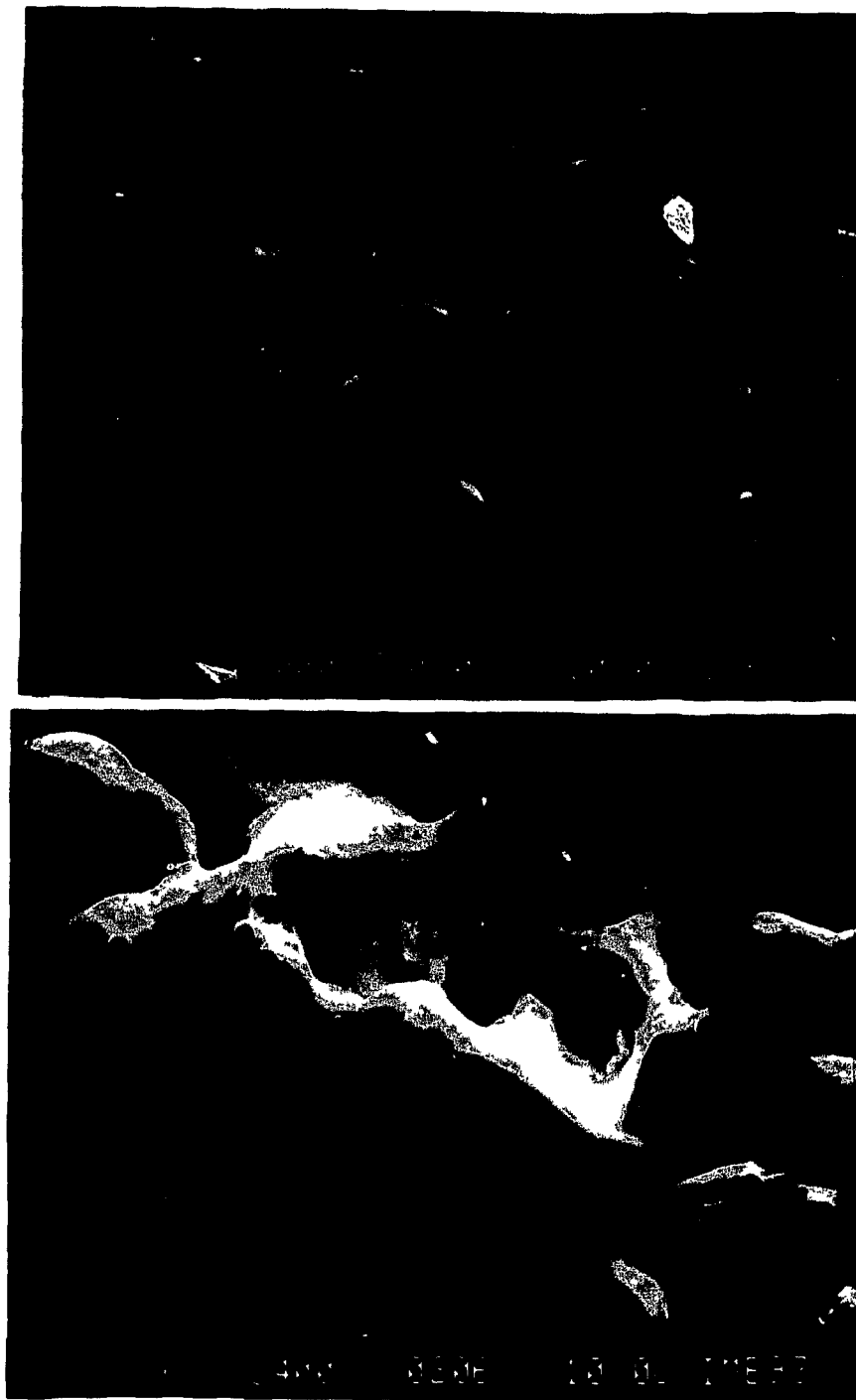


Fig 3.4.2 Scanning electron micrographs of platinum paste directly in contact with the outside of the sensor at magnifications of X1000 and X2400.

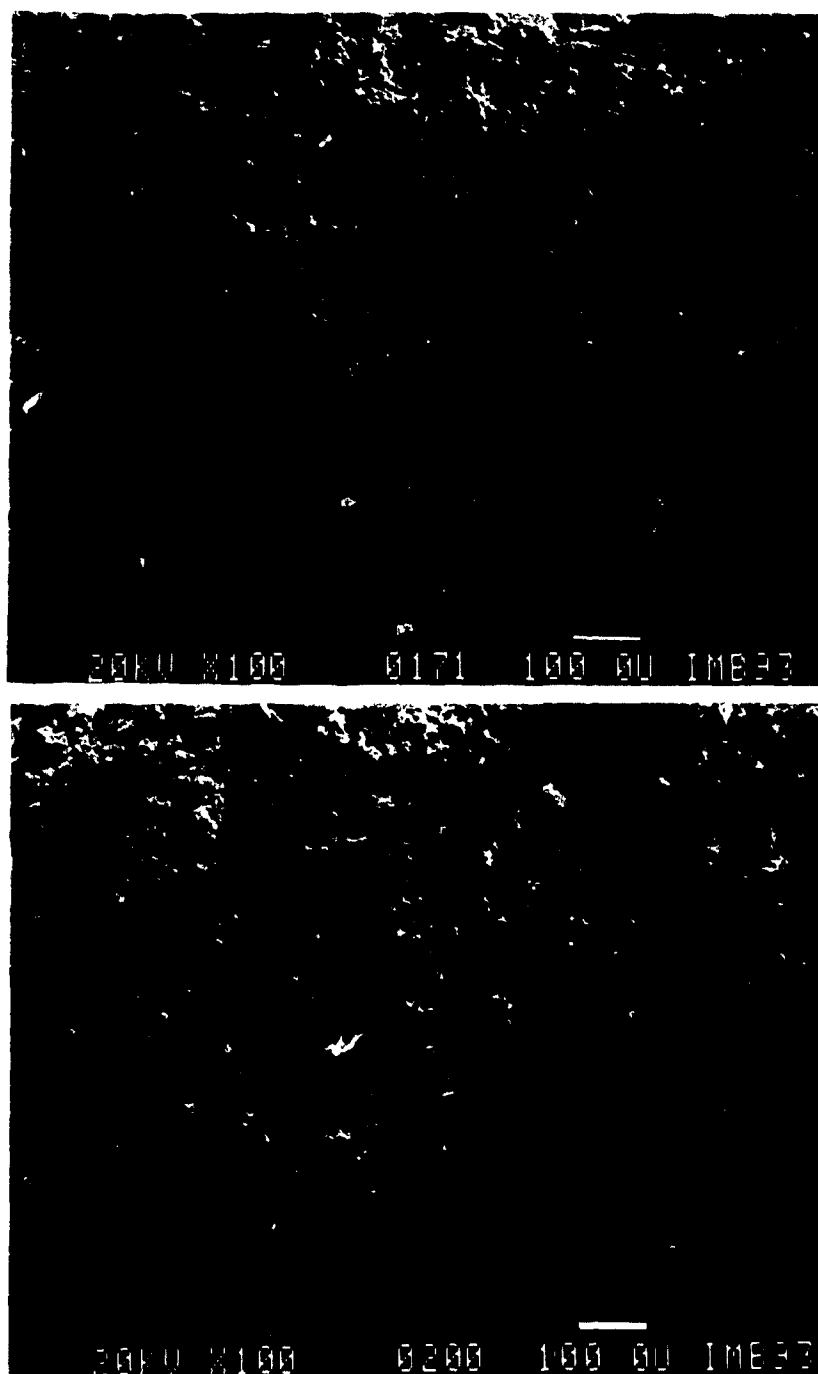


Fig 3.4.3 Scanning electron micrographs of platinum paste in contact with the outside of the sensor at magnifications of X100 at two different positions.

DISCUSSION

4.1 Sensor A

4.1.1 Experimental Observations

The following observations from the Results section need to be explained:

1. A decrease in the response time, $t_{\frac{1}{2}}$, with increase in P_i with an order of about $-\frac{1}{4}$ at low temperature (773 K) for the experiments in which the pressure on the inside of the sensor was changed from high to low.
2. An increase in $t_{\frac{1}{2}}$ with increase in P_i when the pressure in contact with the sensor changed from low to high.
3. An increase in response time with increasing P_i/P_f , as the size of the bulb B' increased for the experiments when the pressure on the inside of the sensor changed from high to low.
4. Faster response in the experiments for which the pressure on the inside of the sensor changed from low to high than in the opposite kind of experiment.
5. The shapes of the experimental traces of voltage vs time.

6. The dependence of the response time on temperature.
7. The dependence of the order of the reaction on temperature, approaching zero at higher temperatures.

4.1.2 Earlier Work

Fouletier et al.²², Anderson and Graves²⁷, Winnubst et al.²⁵, Mogab²⁰ and Mizusaki et al.²⁸ also observed that the response was faster on going from low to high pressure than from high to low pressure. Fouletier et al.²² reported a response time dependence on the inverse square root of the pressure of oxygen. Anderson and Graves did not determine the dependence of response time on pressure or temperature.

4.1.3 A Model for Sensor A:

A model will be proposed for the response of the sensor. Some of the possibilities can be eliminated on the basis of the experimental results.

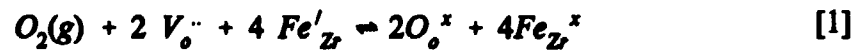
For the overall process, a relaxation time can be defined which is equal to the capacity of a particular reservoir divided by its rate of filling or rate of emptying. An electrical analog is a resistor and a capacitor, the time constant of which is given by C/G where G is the conductance and C is the capacitance. The response time is written as,

Response time $\propto$ Steady state capacity / Rate of filling or emptying.

In the case of a sensor, the steady state capacity is the amount of oxygen that the sensor

can take up until it reaches a steady state and the filling rate is the rate of addition of oxygen to the sensor.

Heyne and Beekmans⁶⁸ suggested several possible causes for the absorption or uptake of oxygen by stabilized zirconia. In a study of the desorption of oxygen from calcia-stabilized zirconia, Dou, Masson and Pacey³⁷ demonstrated that oxygen desorption or uptake is due to the presence of impurities of iron which can have at least three oxidation states. Holes can be trapped at the iron atoms according to the following reaction at higher pressures,



According to the law of mass action, the equilibrium constant for this reaction would be,

$$K_1 = \frac{[O_o^{\cdot}]^2 [Fe_{Zr}^{\cdot}]^4}{P_{O_2} [V_o^{\cdot\cdot}]^2 [Fe'_{Zr}]^4} \quad 4.1$$

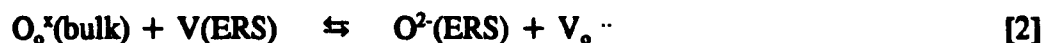
So the concentration of holes at equilibrium would be proportional to the concentration of iron atoms,

$$[h]_{\infty} = [Fe_{Zr}^{\cdot}] = K_1^{1/4} [Fe'_{Zr}] [O_o^{\cdot}]^{-1/2} [V_o^{\cdot\cdot}]^{1/2} P_{O_2}^{1/4} \quad 4.2$$

Here K_1 is the equilibrium constant for reaction [1]. Provided the concentration of vacancies, $[V_o^{\cdot\cdot}]$, and the concentration of oxide anions, $[O^{2-}]$, are so large that they remain virtually unchanged during the absorption or desorption process, and provided the concentration of trapped holes, $[Fe_{Zr}^{\cdot}]$, is very small compared with concentration of

trapping sites, $[\text{Fe}'_{\text{Zr}}]$, then the number of moles of excess oxygen present in a unit volume of the ceramic, considered to be the steady state capacity of the sensor, $[\text{O}_2]_s$ is equal to $[\text{h}]/4$ and is directly proportional to $\text{Po}_2^{1/4}$.

For the experiments when the pressure on the inside of the sensor was changed from high to low, the reaction scheme for the overall process can be written as,



Here ERS stands for the electrochemical reaction site, ads for the adsorption site, bulk for the inside of the electrolyte and g for the gas phase. Step [7] can be replaced by a combination of O and O^- and reaction of O_2^- with h as,



Any one or several of these steps could be rate limiting.

The rate equation for limitation by step 2 would be,

$$\text{Rate} = k_2 [\text{O}_\text{o}^{\cdot-}][\text{V}(\text{ERS})] \quad 4.3$$

$$= k_2 [\text{O}_\text{o}^{\cdot-}](1-\theta_{\text{ERS}}) \quad 4.4$$

where θ_{ERS} is the fraction of electrochemical reaction sites covered, $\text{V}(\text{ERS})$ represents

the vacant electrochemical reaction sites and $[O_v^*]$ is so large that it can be considered as constant.

Considering step 3 as limiting,

$$\begin{aligned} \text{Rate} &= k_3[h(\text{bulk})] \\ &\propto P_{O_2}^{1/4} \end{aligned} \quad 4.5$$

The rate is proportional to the concentration of holes and hence depends on the quarter power of the partial pressure of oxygen according to eq. 4.2. So this elementary step is the diffusion of holes from the bulk of the ceramic to the electrochemical reaction site.

The rate equation for limitation by step [4] is,

$$\begin{aligned} \text{Rate} &= k_4 [O^{2-}(\text{ERS})][h(\text{ERS})] \\ &\propto P_{O_2}^{1/4} \end{aligned} \quad 4.6$$

The concentration of $O^{2-}(\text{ERS})$ is so large that it is assumed to be independent of pressure.

Next, the rate equation for limitation by step [5] is,

$$\text{Rate} = k_5 [O^-(\text{ERS})][h(\text{ERS})] \quad 4.7$$

When reaction [4] is at equilibrium, then

$$K_4 = \frac{[O^-(\text{ERS})]}{[O^{2-}(\text{ERS})][h(\text{ERS})]} \quad 4.8$$

Therefore,

$$[O^-(\text{ERS})] = K_4 [O^{2-}(\text{ERS})][h(\text{ERS})] \quad 4.9$$

Substituting the value of $[O^-(\text{ERS})]$ in the rate equation for reaction [5] will give

$$\text{Rate} = K_4 k_5 [O^{2-}(\text{ERS})][h(\text{ERS})]^2 \quad 4.10$$

$$\propto \text{Po}_2^{1/2}$$

Considering reaction [6] as limiting,

$$\text{Rate} = k_6 [\text{O(ERS)}](1-\Theta_{\text{ads}}) \quad 4.11$$

where Θ_{ads} is the fraction of adsorption surface sites occupied. $[\text{O(ERS)}]$ can be obtained from equations for reactions [4] and [5]. When reaction [5] is at equilibrium, then

$$K_5 = \frac{[\text{O(ERS)}]}{[\text{O}^{2-}(\text{ERS})][\text{h(ERS)}]} \quad 4.12$$

substituting the value of $[\text{O(ERS)}]$ and rearranging, we get

$$[\text{O(ERS)}] = K_5 K_4 [\text{O}^{2-}(\text{ERS})][\text{h(ERS)}]^2 \quad 4.13$$

So the rate for limitation by reaction [6] would be,

$$= k_6 K_4 K_5 [\text{O}^{2-}(\text{ERS})][\text{h(ERS)}]^2 (1-\Theta_{\text{ads}}) \quad 4.14$$

$$\propto \text{Po}_2^{1/2} (1-\Theta_{\text{ads}}) \text{ as } [\text{O}^{2-}(\text{ERS})] \text{ is constant.}$$

$$\propto \text{Po}_2^{1/2}, \text{ if } \Theta_{\text{ads}} \text{ is small.}$$

If reaction [7] is rate limiting, then

$$\text{Rate} = k_7 [\text{O(ads)}]^2 \quad 4.15$$

$$\propto \Theta_{\text{ads}}^2$$

$$\propto \text{Po}_2$$

According to eq. 4.2, the steady state capacity is proportional to $\text{Po}_2^{1/4}$ and according to the first observation for sensor A, the response time is proportional to $\text{Po}_2^{-1/4}$, so the rate of the limiting reaction should be proportional to $\text{Po}_2^{1/2}$. Of all the elementary reactions discussed above, those steps for which the rate is proportional to $\text{Po}_2^{1/4}$ could be rate limiting.⁶⁹ Reactions [5] and [6] have the right order.

In a more mathematical treatment of the proposed model for the behaviour of the sensor, the rate limiting step is selected based on the experimental observations. The reactant in that step or a precursor to that reactant must be considered the dominating reservoir. It is assumed that only one reaction limits the rate of response and that there is only one major reservoir. Both p-jump (where the pressure changed from low to high) and p-drop (where the pressure changed from high to low) experiments have been performed. Therefore, both the forward and the reverse limiting steps must be taken into account. A steady state is reached at the end of the experiment when the rate of the forward process is equal to the rate of the reverse process. The net rate of the reaction would be given as,

$$\phi_i - \phi_{-i}$$

where ϕ_i and ϕ_{-i} are the chemical fluxes⁷⁰ for the i th reaction in the forward and reverse directions. The rate of filling or emptying the reservoir would depend on the net rate of the reaction as,

$$-\frac{d[r]}{dt} = \nu_{r,i} (\phi_i - \phi_{-i}) \quad 4.16$$

where $[r]$ is the concentration of the reservoir species and $\nu_{r,i}$ is the number of reservoir species reacting each time that reaction i takes place.

On integrating the above differential equation, the concentration of the reservoir species will be obtained. This can be inserted into the Nernst equation to get the instantaneous voltage. This procedure will be explained by taking reactions [3], [5], and [6] as limiting with various reservoirs.

4.1.4 Reaction [5] as rate limiting

Reaction [5] is written as,



In this reaction $[\text{O}^-(\text{ERS})]$ and $[\text{h}(\text{ERS})]$ are variable and $[\text{O}(\text{ERS})]$ is constant since as soon as it is formed it is equilibrated in the subsequent reaction which is assumed to be fast. $[\text{O}(\text{ERS})]$ actually changes as a step function. It starts in equilibrium with P_i and ends in equilibrium with P_f . The constant, final value of $[\text{O}(\text{ERS})]$ can be written as $[\text{O}(\text{ERS})]_\infty$. It is also assumed that the steps occurring before the rate limiting step are in equilibrium with the reactants in the rate limiting step. Therefore $[\text{O}^-(\text{ERS})]$ can be expressed in terms of $[\text{h}(\text{ERS})]$.

Assuming that reaction [4] is at equilibrium, the equilibrium constant K_4 is given by eq. 4.8 as,

$$K_4 = \frac{[\text{O}^-(\text{ERS})]}{[\text{h}(\text{ERS})][\text{O}^{2-}(\text{ERS})]}$$

where K_4 is the equilibrium constant for reaction 4 and $[\text{O}^{2-}(\text{ERS})]$ is constant so $[\text{h}(\text{ERS})] \propto [\text{O}^-(\text{ERS})]$. $[\text{O}^-(\text{ERS})]$ can be calculated from the above equation as in eq. 4.9,

$$[\text{O}^-(\text{ERS})] = K_4 [\text{h}(\text{ERS})][\text{O}^{2-}(\text{ERS})]$$

If holes are considered as the major reservoir then substituting the appropriate species

in eq. 4.16, one obtains the differential rate equation for reaction [5] as,

$$-\frac{d[h(ERS)]}{dt} = 2(k_3[O^-(ERS)][h(ERS)] - k_{-3}[O(ERS)]_{\infty}) \quad 4.17$$

where k_3 is the rate constant for the forward reaction and k_{-3} is the rate constant for the reverse reaction, $k_3[O^-(ERS)][h(ERS)]$ is the chemiflux for the forward reaction and $k_{-3}[O(ERS)]_{\infty}$ is the chemiflux for the reverse reaction. Reaction [4] also occurs and removes another hole every time that reaction [5] occurs, for a total stoichiometric factor for holes of two.

Separating the variables in eq. 4.17, one obtains,

$$-\frac{d[h(ERS)]}{k_3[O^-(ERS)][h(ERS)] - k_{-3}[O(ERS)]_{\infty}} = 2 dt \quad 4.18$$

After reaction [5] reaches equilibrium, the rate of the forward and reverse reactions would be equal,

$$k_3[O^-(ERS)]_{\infty}[h(ERS)]_{\infty} = k_{-3}[O(ERS)]_{\infty} \quad 4.19$$

Substituting the values of $k_{-3}[O(ERS)]_{\infty}$ from eq. 4.19 and $[O^-(ERS)]$ from eq. 4.9 in eq. 4.18, we get

$$-\frac{d[h(ERS)]}{K_4 k_3 [O^{2-}(ERS)][h(ERS)]^2 - K_4 k_3 [O^{2-}(ERS)][h(ERS)]_{\infty}^2} = 2 dt \quad 4.20$$

For the pressure drop experiments, rearranging the above equation would give,

$$- \frac{d[h(ERS)]}{[h(ERS)]^2 - [h(ERS)]_{\infty}^2} = 2k_3K_4[O^{2-}(ERS)] dt \quad 4.21$$

Integrating between the limits $[h(ERS)] = [h(ERS)]_0$ at $t=0$ and $[h(ERS)] = [h(ERS)]$ at $t=t$, one obtains

$$- \int_{[h(ERS)]_0}^{[h(ERS)]} \frac{d[h(ERS)]}{[h(ERS)]^2 - [h(ERS)]_{\infty}^2} = \int_0^t 2K_4k_3[O^{2-}(ERS)] dt \quad 4.22$$

Using the table of integrals⁷¹, the following expression is obtained,

$$\coth^{-1} \frac{[h(ERS)]}{[h(ERS)]_{\infty}} - \coth^{-1} \frac{[h(ERS)]_0}{[h(ERS)]_{\infty}} = 2tK_4k_3[O^{2-}(ERS)][h(ERS)]_{\infty} \quad 4.23$$

Now,

$$\coth^{-1}(x) = \tanh^{-1}(1/x) \quad 4.24$$

On rearrangement eq. 4.23 would give,

$$\frac{[h(ERS)]}{[h(ERS)]_{\infty}} = \coth \left[\tanh^{-1} \frac{[h(ERS)]_{\infty}}{[h(ERS)]_0} + 2K_4k_3[h(ERS)]_{\infty}[O^{2-}(ERS)] t \right] \quad 4.25$$

The Nernst equation in terms of electron holes gives the change in cell voltage,

$$\Delta E = \frac{RT}{F} \ln \frac{[h]}{[h]_0} \quad 4.26$$

From eq. 4.2, $[h]$ is proportional to $PO_2^{1/4}$ so its concentrations in the steady states at the beginning and the end of the experiment would be,

$$\frac{[h]_{\infty}}{[h]_0} = \left[\frac{P_f}{P_i} \right]^{1/4} \quad 4.27$$

Here P_i and P_f are the initial and final pressures in the experiment.

Substituting these values in the Nernst equation, we get

$$\Delta E = \frac{RT}{F} \ln \left[\left(\frac{P_f}{P_i} \right)^{1/4} \coth \left[\tanh^{-1} \left(\frac{P_f}{P_i} \right)^{1/4} + 2 t K_4 k_5 [h(ERS)]_{\infty} [O^{2-}(ERS)] \right] \right] \quad 4.28$$

This equation shows a correct dependence on the order given in Table 3.1.7 and shown in Figs. 3.1.4 and 3.1.5. In eq. 4.28, as $\coth(x) = (1 + e^{-2x})/(1 - e^{-2x})$, the exponential term can be considered as $\exp(-t/\tau)$, where τ depends upon the inverse of the concentration of holes, $[h(ERS)]_{\infty}$, which shows a quarter-power dependence on the partial pressure of oxygen. Hence response time will show an inverse dependence on the quarter power of the partial pressure of oxygen.

For the experiments in which the pressure on the inside of the sensor was changed from low to high, the differential rate equation would be,

$$-\frac{d[h(ERS)]}{dt} = 2(k_5[O^{2-}(ERS)][h(ERS)] - k_{-5}[O(ERS)]_{\infty}) \quad 4.29$$

For the p-jump experiments, $[h(ERS)]_{\infty} > [h(ERS)]$ as $P_f > P_i$ so eq. 4.21 would be written as,

$$\frac{d[h(ERS)]}{[h(ERS)]_{\infty}^2 - [h(ERS)]^2} = 2k_3K_4[O^{2-}(ERS)] dt \quad 4.30$$

This is integrated between the limits $[h(ERS)] = [h(ERS)]_0$ at $t=0$ and $[h(ERS)] = [h(ERS)]$ at $t=t$,

$$\int_{[h(ERS)]_0}^{[h(ERS)]} \frac{d[h(ERS)]}{[h(ERS)]_{\infty}^2 - [h(ERS)]^2} = \int_0^t 2K_4k_3[O^{2-}(ERS)] dt \quad 4.31$$

The following expression is obtained using Tables of integrals⁷¹,

$$\tanh^{-1} \frac{[h(ERS)]}{[h(ERS)]_{\infty}} - \tanh^{-1} \frac{[h(ERS)]_0}{[h(ERS)]_{\infty}} = 2tK_4k_3[O^{2-}(ERS)][h(ERS)]_{\infty} \quad 4.32$$

On rearrangement this would give,

$$\frac{[h(ERS)]}{[h(ERS)]_{\infty}} = \tanh \left[\tanh^{-1} \frac{[h(ERS)]_0}{[h(ERS)]_{\infty}} + 2K_4k_3[h(ERS)]_{\infty}[O^{2-}(ERS)] t \right] \quad 4.33$$

This can be rearranged as,

$$\frac{[h(ERS)]_0}{[h(ERS)]} = \frac{[h(ERS)]_0}{[h(ERS)]_{\infty}} \coth \left[\tanh^{-1} \frac{[h(ERS)]_0}{[h(ERS)]_{\infty}} + 2K_4k_3[h(ERS)]_{\infty}[O^{2-}(ERS)] t \right] \quad 4.34$$

The Nernst equation for this experiment can be written as,

$$\Delta E = \frac{RT}{F} \ln \frac{[h]_0}{[h]} \quad 4.35$$

Substituting the values in the Nernst equation, we get

$$\Delta E = \frac{RT}{F} \ln \left[\left(\frac{P_i}{P_f} \right)^{1/4} \coth \left[\tanh^{-1} \left(\frac{P_i}{P_f} \right)^{1/4} + 2 \left(K_4 k_5 [h(ERS)] [O^{2-}(ERS)] \right) \right] \right]$$

4.36

4.1.5 Reaction [6] as rate limiting

Now we will consider reaction [6] as an example of a rate limiting reaction.

Reaction [6] can be written as,



In this example, only the coverage at the adsorption sites is considered. The coverage at electrochemical sites is not taken into account.

The differential rate equation for this reaction can be written as,

$$- \frac{d[O(ERS)]}{dt} = k_6 [O(ERS)] (1 - \theta_{ads}) - k_{-6} \theta_{ads} \quad 4.37$$

where θ_{ads} is the fraction of surface covered by O(ads). Here O(ERS) will be considered as the reservoir as an example. The concentration of O(ads) would stay constant as it would rapidly equilibrate with the species in the subsequent reactions.

The variables are separated and the result is integrated between the limits from

$[O(ERS)] = [O(ERS)]_0$ at $t=0$ and $[O(ERS)] = [O(ERS)]$ at $t=t$.

$$- \int_{[O(ERS)]_0}^{[O(ERS)]} \frac{d[O(ERS)]}{k_6[O(ERS)](1-\theta_{ads}) - k_{-6}\theta_{ads}} = \int_0^t dt \quad 4.38$$

The integrated equation is,⁷¹

$$\ln \left[\frac{k_6(1-\theta_{ads})[O(ERS)] - k_{-6}\theta_{ads}}{k_6(1-\theta_{ads})[O(ERS)]_0 - k_{-6}\theta_{ads}} \right] = -k_6 t (1-\theta_{ads}) \quad 4.39$$

At equilibrium ($t = \infty$),

$$k_6(1-\theta_{ads})[O(ERS)]_{\infty} = k_{-6}\theta_{ads} \quad 4.40$$

Substituting the value of k_{-6} in eq. 4.39, we obtain,

$$\ln \left[\frac{k_6(1-\theta_{ads})[O(ERS)] - k_6(1-\theta_{ads})[O(ERS)]_{\infty}}{k_6(1-\theta_{ads})[O(ERS)]_0 - k_6(1-\theta_{ads})[O(ERS)]_{\infty}} \right] = -t k_6 (1-\theta_{ads}) \quad 4.41$$

On rearrangement the following expression is obtained,

$$\frac{[O(ERS)] - [O(ERS)]_{\infty}}{[O(ERS)]_0 - [O(ERS)]_{\infty}} = e^{-t k_6 (1-\theta_{ads})} \quad 4.42$$

Therefore,

$$\frac{[O(ERS)]}{[O(ERS)]_o} = \left[1 - e^{-k_d(1-\theta_{ads})}\right] \frac{[O(ERS)]_s}{[O(ERS)]_o} + e^{-k_d(1-\theta_{ads})} \quad 4.43$$

The products of the rate limiting reactions are in equilibrium with O_2 via the subsequent fast reactions. A combination of reactions [7] and [8] can be expressed as,



The value of θ_{ads} can be calculated from reaction [11] as,⁷²

$$\theta_{ads} = \frac{K_{11}^{-1/2} P_{O_2}^{1/2}}{1 + K_{11}^{-1/2} P_{O_2}^{1/2}} \quad 4.44$$

where K_{11} is the equilibrium constant for reaction [11].

The Nernst equation in terms of $[O(ERS)]$ is,

$$\Delta E = \frac{RT}{2F} \ln \frac{[O(ERS)]}{[O(ERS)]_o} \quad 4.45$$

On substituting the values and performing the necessary algebra this becomes

$$\Delta E = \frac{RT}{2F} \ln \left[\left(\frac{P_i}{P_o}\right)^{1/2} \left[1 - e^{-k_d(1+K_{11}^{-1/2} P_{O_2}^{1/2})}\right] + e^{-k_d(1+K_{11}^{-1/2} P_{O_2}^{1/2})} \right] \quad 4.46$$

According to this equation, the response time would be proportional to $PO_2^{1/2}$ if the term $K_{11}^{-1/2} PO_2^{1/2}$ is larger and will be independent of pressure if this term is smaller.

4.1.6 Reaction [3] as rate limiting

At higher temperatures, the order of $t_{1/2}$ with respect to P_i approached zero (Table 3.1.7), so according to the relationship between capacity, response time and the filling rate, elementary reactions for which the rate is proportional to $P_{O_2}^{1/4}$ would be considered rate limiting if the reservoir is the electron holes. These steps could be the diffusion of holes, reaction [3], or the reaction between the oxide anions and the holes, reaction [4].

If reaction [3] is considered to be rate limiting,



the rate would be proportional to the concentration of holes, $[h(a)]$ which is proportional to the quarter power of the partial pressure of oxygen, $P_{O_2}^{1/4}$. Here (a) and (b) refer to the bulk and ERS, respectively.

The differential rate equation for reaction [3] can be written as,

$$-\frac{d[h(a)]}{dt} = k_3[h(a)] - k_{-3}[h(b)] \quad 4.47$$

where k_3 is the rate constant for the forward process and k_{-3} is the rate constant for the reverse process. Since the reactions following the rate-limiting step are considered to be fast, $[h(b)]$ would be constant after the initial change, because as soon as it is formed it would be equilibrated with O_2 by the subsequent reactions. In the steady state,

$$k_3[h(a)]_{ss} = k_{-3}[h(b)]_{ss} \quad 4.48$$

Separating the variables in eq. 4.47 and substituting the value of $k_{-3}[h]_{ss}$, we obtain,

$$-\frac{d[h(a)]}{k_3[h(a)] - k_3[h(a)]_\infty} = dt \quad 4.49$$

Integrating between the limits $[h]_0$ at $t=0$ and $[h]$ at $t=t$ using Tables of integrals⁷¹ and rearranging,

$$\frac{[h(a)] - [h(a)]_\infty}{[h(a)]_0 - [h(a)]_\infty} = \exp(-k_3 t) \quad 4.50$$

where $[h(a)]$ is the concentration of holes at time t , $[h(a)]_0$ is the concentration in the beginning and $[h(a)]_\infty$ is the concentration of holes at the steady state. On rearrangement of this equation, we get,

$$\frac{[h(a)]}{[h(a)]_0} = \frac{[h(a)]_\infty}{[h(a)]_0} (1 - e^{-k_3 t}) + e^{-k_3 t} \quad 4.51$$

The Nernst equation in terms of electron holes would be,

$$\Delta E = \frac{RT}{F} \ln \frac{[h(a)]}{[h(a)]_0} \quad 4.52$$

On substituting the values from eq. 4.51, an expression for the change of voltage is obtained

$$\Delta E = \frac{RT}{F} \ln \left[\left[\frac{P_f}{P_i} \right]^{1/4} (1 - e^{-k_3 t}) + e^{-k_3 t} \right] \quad 4.53$$

This equation gives the right order of zero as the exponential term does not depend on the concentration of any species.

4.1.7 General Forms of the Equations

Eqs. 4.28, 4.36, 4.46 and 4.53 give the integrated rate laws for some limiting steps. The rate laws for various other possible limiting steps and reservoirs have been integrated and it was found that most cases can be described by one or the other of two general equations. The general forms of these equations are,

$$E = \frac{RT}{nF} \ln [A + (1-A)e^{-Bt}] \quad 4.54$$

$$E = \frac{RT}{nF} \ln [A \coth(\tanh^{-1}A + Bt)] \quad 4.55$$

Eq. 4.54 is applicable where only one reservoir species is involved in the rate limiting step and eq. 4.55 where two species from the reservoir combine in the limiting step.

For eq.4.54, A equals $(P_f/P_i)^x$ and for eq.4.55, A equals $(P'/P'')^x$, where P' is the smaller of the initial and the final pressures and P'' is the bigger of these pressures. The value of x depends on the composition of the species in the reservoir and can be $1/4$, $1/2$ or 1 as explained below.

At the steady state at the beginning and end of the experiment, according to eq. 4.27,

$$\frac{[h]_{\infty}}{[h]_0} = \left[\frac{P_f}{P_i} \right]^{1/4}$$

So the value of x will be $1/4$ for holes (h , $Fe_{Zr}^{\cdot}$ or $O^{\cdot}$). The value of x will be $1/2$ for

atomic oxygen as,

$$\frac{[O]_{\infty}}{[O]_0} = \left[\frac{P_f}{P_i} \right]^{1/2} \quad 4.56$$

and x will be unity for molecular oxygen as,

$$\frac{[O_2]_{\infty}}{[O_2]_0} = \frac{P_f}{P_i} \quad 4.57$$

In the denominator of eqs. 4.54 and 4.55, n is the number of charges in the reservoir species and is equal to 4x.

The parameter B equals the stoichiometric coefficient of the reservoir species in the limiting step times the chemiflux of the limiting reaction divided by the concentration of the reservoir species as follows,

$$B = \nu_{r,l} \phi_{l,\infty} / [r]_{\infty} \quad 4.58$$

B is proportional to the rate constant of the limiting reaction step involved and to any equilibrium constants required to relate the concentration of the reservoir species to the reactant in the limiting step.

As stated earlier, the rate laws for other limiting steps have also been integrated. Table 4.1 lists the various possible limiting steps with various reservoirs, the form of the integrated rate equations and the forms of x and B.

Table 4.1 Forms of the integrated rate equations for some possible limiting steps

Limiting reaction	Reservoir	Form of eq.	x	B
$h(a) \rightleftharpoons h(b)$	h	4.54	$\frac{1}{4}$	k_3
$O^{2-}(b) + h(b) \rightleftharpoons O^-(b)$	h	4.54	$\frac{1}{4}$	$k_4[O^{2-}]$
$O^-(b) + h(b) \rightleftharpoons O(b)$	h	4.55	$\frac{1}{4}$	$k_5 K_4 [h]_{\infty} [O^{2-}]$
$O(b) + V(ad) \rightleftharpoons O(ad)$	O(b)	4.54	$\frac{1}{2}$	$k_6 / (1 + K_{11}^{-1/2} P_{O_2}^{1/2})$
$2O(ad) \rightleftharpoons O_2(ad)$	O(ad)	4.55	$\frac{1}{2}$	$k_3 [O(ad)]_{\infty}$
$O_2(ad) \rightleftharpoons O_2(g) + V(ad)$	O ₂	4.54	1	k
$O(b) + V(ad) \rightleftharpoons O(ad)$	h	4.55	$\frac{1}{4}$	$k_6 K_5 K_4 [h]_{\infty} [O^{2-}] (1-\theta)$
$2O^-(b) \rightleftharpoons$ $O_2^{2-}(b) + e^- + V(b)$	h	4.55	$\frac{1}{4}$	$K_3 k_4 [h(b)]_{\infty} [O^{2-}]$
$O^-(b) + O(ad) + h(b) \rightleftharpoons$ $O_2(g) + V(b)$	O ⁻	4.55	$\frac{1}{4}$	$\frac{k_4 [O^-(b)]_{\infty}}{K_3 [O^{2-}(b)]}$

In this Table, a stands for bulk, b for ERS and ad for adsorption sites.

4.1.8 Behaviour of the Sensor at 773 K

Now we will consider each general form of the integrated rate equations and see which can explain all the experimental observations at a particular temperature.

In eq. 4.55 , when t equals 0, Bt equals 0 and hence E equals 0. When $t = \infty$, then eq. 4.55 becomes,

$$\Delta E_{\infty} = \frac{RT}{4F} \ln \frac{P_f}{P_i} \quad 4.59$$

which is the Nernst equation used in our experimental calculations.

The response time, is the time when $\Delta E = \Delta E_{\infty}/2$, and dividing the above equation by 2 will give the value of $\Delta E_{1/2}$ as follows,

$$\Delta E_{1/2} = \frac{RT}{8F} \ln \frac{P_f}{P_i} \quad 4.60$$

On inserting the value of this voltage in eq 4.55 and solving for time would give the response time as

$$t_{1/2} = \frac{1}{2B} \ln \left[\frac{1 - A^{3/2} - A + A^{1/2}}{1 - A^{3/2} + A - A^{1/2}} \right] \quad 4.61$$

The various experimental observations at low temperature (773 K) can be explained with the predictions of eq. 4.55 as follows,

1. For the experiments in which the pressure was changed from high to low, the response

time showed an inverse dependence on $P_i^{1/4}$. For these experiments when P_i was changed, P_f changed proportionately and the ratio P_i/P_f remained the same for all values of P_i thus the response time depended on P_f too. For reaction [5] as the limiting step and electron holes as the reservoir, the parameter B is,

$$B = K_4 k_5 [O^2(ERS)][h(ERS)]_{\infty} \quad 4.62$$

In eq. 4.61, $t_{1/2}$ is inversely proportional to B which is related to $[h(ERS)]_{\infty}$ and hence to $P_f^{1/4}$. As the value of parameter A will remain the same on changing P_i (because the ratio P_i/P_f will stay the same), the value of $t_{1/2}$ will not be affected by the logarithmic factor in eq. 4.61. This explains the inverse dependence of the response time on the quarter power of P_i or P_f .

2. For the experiments when the pressure on the inside of the sensor changed from low to high, the final pressure P_f was constant at atmospheric pressure and $t_{1/2}$ would only be affected by the weaker logarithmic factor in eq. 4.61. On putting the appropriate values in eq. 4.61, it is found that $t_{1/2}$ would increase slightly with increasing P_i . This was observed experimentally.

3. This also explains the faster response of the sensor when the size of the expansion bulb in the equipment was made smaller. The ratio P_i/P_f became closer to unity on decreasing the size of the bulb. Since the initial pressure in these experiments remained the same the faster response was mainly due to the increase in the value of the final pressure. The parameter B increases with increasing value of P_f , and since B is inversely

proportional to $t_{1/2}$, therefore response time would decrease with increasing P_f . The value of P_f/P_i also affects A and hence $t_{1/2}$ but this dependence is weaker than the dependence on P_f .

4. There was faster response of the sensor when the pressure change was from low to high than from high to low for the same pressure ratio because in the former experiment the value of P_f was higher which made B larger and hence the response faster.

5. Parameter B was obtained by fitting eq. 4.55 to the experimental traces of voltage vs time at 773 K using nonlinear least squares.⁶⁷ The value of P_f/P_i was taken from the experimental data. The points were read off from the experimental curves of voltage vs time and were used as an input for the BMDP computer program.⁶⁷ Examples of such fits are shown in Figs. 4.1 and 4.2 and the value of the parameters obtained by fitting are given in Table 4.2. In these figures, the solid line is the experimental trace and the points are the theoretical values. The values of the square root of the mean square deviation (SRMSD) between experimental and theoretical results are also given in Table 4.2 and are similar to the experimental noise level.

Response times, were calculated using eq. 4.61 with the values of the parameter B obtained from the curve fits and P_f/P_i from the experiment. Both the experimental and the calculated values obtained are given in Table 4.2 and match very well. The average difference is 1.8 s and the maximum difference is 4 s.

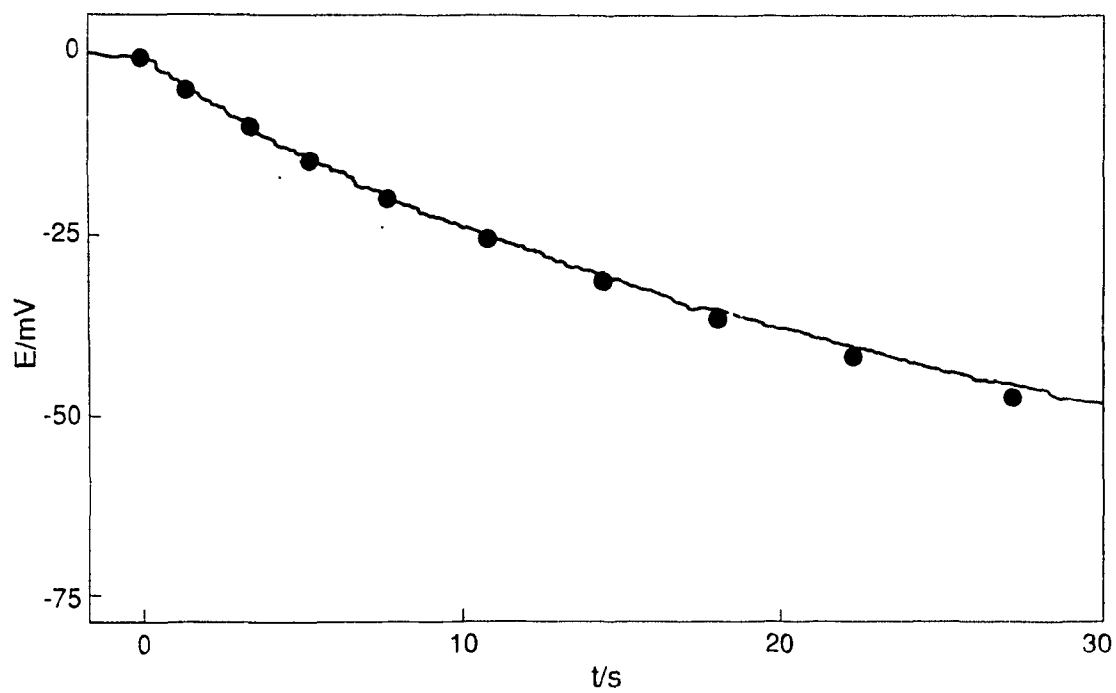


Fig 4.1 Sensor output voltage with respect to time for a pressure change from 761 torr to 8.3 torr at 773 K. -, experiment; ● fit of eq. 4.55 to the data.

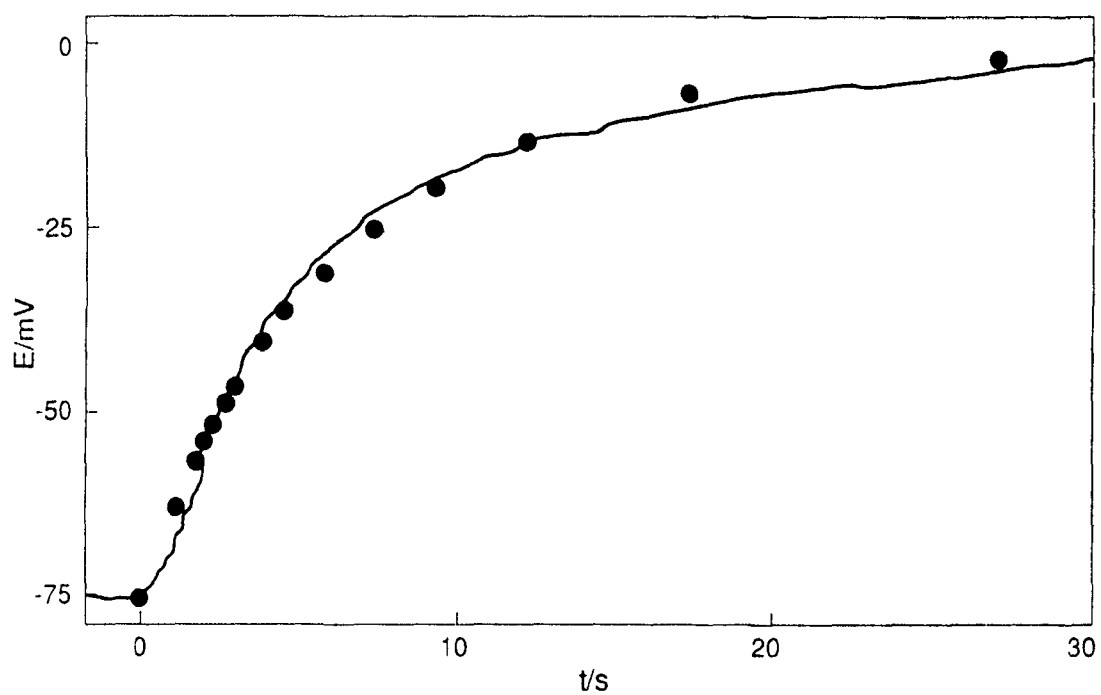


Fig 4.2 Sensor output voltage with respect to time for a pressure change from 8.2 torr to 761 torr at 773 K. -, experiment; ● fit of eq. 4.55 to the data.

Table 4.2. Results of nonlinear least squares fits of eq. 4.55 to experimental voltage-time curves at 773 K.

P_i	P_f	$t_{1/2}$	$B \cdot 10^2$	SRMSD	$t_{1/2}$
		expt			calc
torr	torr	s	s^{-1}	mV	s
717	8.5	23	1.38 ± 0.03	1.2	23
761	8.3	21	1.58 ± 0.02	0.8	20
8.2	761.4	3.8	6.76 ± 0.27	2.9	4.6
758	33.3	34	0.95 ± 0.03	1.3	34
209	9.2	45	0.74 ± 0.04	2.2	44
760	5.5	62	0.47 ± 0.01	2.0	65
758	25.1	38	0.78 ± 0.02	1.2	42
759	49.6	26	1.2 ± 0.1	1.7	28
450	741.6	30	1.2 ± 0.1	0.7	29
177	733.2	22	1.4 ± 0.1	1.6	25
52.3	730.6	19	1.64 ± 0.13	3.2	20
754	48.9	47	0.69 ± 0.04	3.1	49
490	31.6	53	0.59 ± 0.03	1.7	57

4.1.9 Response of Sensor A at Higher Temperatures

In order to explain the behaviour of the sensor at higher temperatures, we consider eq. 4.54. In this equation, when t equals 0, $\exp(-Bt)$ equals 1 and hence E equals 0. When t approaches infinity, eq.4.54 becomes equal to the Nernst equation. When the voltage reaches half the theoretical Nernstian value,

$$\Delta E_{1/2} = \frac{RT}{4F} \ln \left[\frac{P_f}{P_i} \right]^{1/2} \quad 4.63$$

For eq. 4.54,

$$\Delta E_{1/2} = \frac{RT}{F} \ln \left[A + (1-A)e^{-Bt_{1/2}} \right] \quad 4.64$$

So the value of $t_{1/2}$ can be obtained from eq. 4.64, as

$$t_{1/2} = \frac{1}{B} \ln \left[\frac{1-A}{A^{1/2}-A} \right] \quad 4.65$$

The various observations are explained as follows:

1. The order of the reaction at higher temperatures approaches zero and $t_{1/2}$ shows an inverse dependence on B in eq. 4.65. B for reaction [3] is equal to the rate constant of the limiting reaction step and B for reaction [4] is equal to the rate constant times $[O^2- (ERS)]$. Since B is independent of the partial pressure of oxygen, $t_{1/2}$ does not change with changing pressure.
2. The values of the parameter B were determined by fitting eq. 4.54 to the experimental

traces of voltage vs time at higher temperatures. The values of the parameter B and of the square root of the mean square deviation (SRMSD) are given in Table 4.3. These experimental traces were also fitted to eq. 4.55. This gave a higher value of SRMSD as listed in Table 4.3 which suggests that eq. 4.54 is more suitable for describing reaction [3] or [4] as the rate limiting step at higher temperatures. The value of $t_{1/2}$ was calculated using eq. 4.65 with the value of the parameter obtained from the curve fitting and P/P_i from the experiment. These are given in Table 4.4 and agree very well with the experimental values.

4.1.10 Arrhenius Parameters

Arrhenius parameters can be derived for the elementary step 5. In a study of the permeation of oxygen through calcia-stabilized zirconia at 1233 to 1723 K, Dou et.al.⁷³ observed that the flux of oxygen through a surface depends on the oxygen pressure as,

$$J = \frac{1}{4} \alpha P_{O_2}^{1/2} \quad 4.66$$

where α is the surface reaction parameter and is given as,

$$\ln \alpha \text{ (mol cm}^{-2}\text{s}^{-1}\text{atm}^{-1/2}\text{)} = -(0.690 \pm 0.437) - \frac{191 \pm 5 \text{ kJ mol}^{-1}}{RT} \quad 4.67$$

Table 4.3 Results of nonlinear least squares fits of eqs. 4.54 and 4.55 to experimental voltage-time curves at three temperatures.

T	P_i	P_f	B Eq.4.54	SRMSD	B Eq.4.55	SRMSD
(K)	torr	torr	s⁻¹	mV	s⁻¹	mV
848	749	49	3.37±0.12	2.0	1.34±0.19	12.8
873	756	5.3	2.55±0.12	5.6	0.57±0.05	13.2
923	758	5.3	2.76±0.15	6.9	0.62±0.06	14.9

Table 4.4 Comparison of response times obtained experimentally and using eq. 4.65.

T (K)	t_½, expt	t_½, calc
	s	s
848	0.26	0.26
873	0.44	0.41
923	0.40	0.38

In eq. 4.66, the flux is related to the square root of the partial pressure of oxygen. In the mechanism proposed above, in order for an elementary step to be rate limiting at 773 K, its rate should show a square root dependence on the partial pressure of oxygen. So the dependence in eq. 4.66 of the flux on the pressure matches this criterion although the temperature was higher than our experimental temperatures.

The flux can be expressed in terms of the chemiflux of holes as

$$\Phi_{s,\infty} = \alpha P_{o_2}^{1/2} \quad 4.68$$

For reaction [5], parameter $B = 2 \phi_{s,\infty} / [h]_{\infty}$.

Substituting the value of $\phi_{s,\infty}$ from eq. 4.68 and $[h]_{\infty}$ from eq. 4.2, parameter B for reaction [5] can be written as,

$$B = 2 \alpha K_1^{-1/4} [Fe'_{Zr}]^{-1} [O_o]^{1/2} [V_o]^{-1/2} P_{o_2}^{1/4} \quad 4.69$$

This can be substituted in eq. 4.61, and we get

$$\frac{1}{t_{1/2}} = 4 \alpha K_1^{-1/4} [Fe'_{Zr}]^{-1} [O_o]^{1/2} [V_o]^{-1/2} P_{o_2}^{1/4} \ln \left[\frac{1 - A^{3/2} + A - A^{1/2}}{1 - A^{3/2} - A + A^{1/2}} \right] \quad 4.70$$

Differentiating the above eq.4.70 with respect to temperature at constant pressure we get,

$$\frac{d \ln(1/t_{1/2})}{dT} = \frac{d \ln \alpha}{dT} - \frac{1}{4} \frac{d \ln K_1}{dT} \quad 4.71$$

The activation energy would be,

$$E_A = E_{A\alpha} - \frac{\Delta H_1}{4} \quad 4.72$$

where E_A is the activation energy of the response rate, $E_{A\alpha}$ is the activation energy for the surface limited desorption and ΔH_1 is the enthalpy of the overall absorption reaction. The value of $E_{A\alpha}$ for calcia-stabilized zirconia obtained experimentally was $191 \pm 5 \text{ kJ mol}^{-1}$ ⁷³ and the experimental value of ΔH_1 was $-148 \pm 53 \text{ kJ mol}^{-1}$.³⁷ These values were substituted in eq. 4.72 to obtain the value of E_A which was found to be $228 \pm 14 \text{ kJ mol}^{-1}$. This matches reasonably well with the activation energy of $210 \pm 14 \text{ kJ mol}^{-1}$ obtained experimentally for sensor A. This indicates that a possible mechanism would be limitation by surface reaction on zirconia with holes as a reservoir.

Now the pre-exponential factor can be compared. In eq. 4.70, α is replaced by its pre-exponential factor, $\exp(-0.690 \pm 0.437) \text{ mol cm}^{-2}\text{s}^{-1}\text{atm}^{-1/4}$ for calcia-stabilized zirconia. The equilibrium constant for reaction [1] is written as,

$$K_1 = \exp \left[\frac{\Delta S_1}{R} - \frac{\Delta H_1}{RT} \right] \quad 4.73$$

Assuming $[O_o^{\bullet}]/[V_o^{\bullet}]$ equal to unity at 1 atm pressure, the entropy change for reaction [1] was found to be $-141 \pm 35 \text{ J K}^{-1}\text{mol}^{-1}$.³⁷ Substituting this value of ΔS_1 and R in eq. 4.73 at infinite temperature gives K_1^{∞} equal to $\exp(\Delta S_1/4R)$. Therefore the expression for the pre-exponential factor, A' , will be,

$$A' = 4e^{-0.690 \pm 0.437} e^{-\frac{\Delta S_1}{4R}} [Fe']^{-1} [O_2]^{1/2} [V_o']^{-1/2} P_{O_2}^{1/4} \ln \left[\frac{1 - A^{3/2} + A - A^{1/2}}{1 - A^{3/2} - A + A^{1/2}} \right] \quad 4.74$$

The TOSOH powder used for making the sensors contained 0.004 wt % Fe_2O_3 . The density of 8 mol % yttria-stabilized zirconia is 6 g ml^{-1} .⁷⁴ So the concentration of iron, $[Fe]$ equalled 3.0×10^{-6} moles ml^{-1} .

The value of A was calculated from the initial and final pressures in the experiment.

Substituting all the values in the equation for the pre-exponential factor, the value of A' times some distance comes out to be $10^{7.0 \pm 0.5}$ cm s^{-1} . Now we have to find out what this distance is.

In order to express the concentration of iron in moles per unit area, its concentration per unit volume 3.0×10^{-6} moles cm^{-3} is divided by the effective thickness of the reservoir layer. For 8 mol% yttria-stabilized zirconia, one monolayer would be 3.24×10^{-8} cm thick. If the reaction is assumed to take place in one monolayer of zirconia, then the pre-exponential factor comes out to be $10^{14.5 \pm 0.5}$ s^{-1} which is an order of magnitude more than the experimental value of $10^{12.8 \pm 0.9}$ s^{-1} .

The size of the Pt grains as observed in the SEM micrographs for the electrode were from 0.5 to 8 microns. If the reaction occurs under the Pt grains then this gives a pre-exponential factor of 10^{11} s^{-1} . The size of the platinum grains directly in contact with

the zirconia was observed to be 0.90 ± 0.37 microns. This would give a pre-exponential factor of $10^{11.4 \pm 0.7} \text{ s}^{-1}$ which agrees better with the experimental value of $10^{12.8 \pm 0.9} \text{ s}^{-1}$.

The distance between the various electrode/electrolyte contacts was about 10 microns, which gives a pre-exponential factor of 10^{10} s^{-1} . This suggests that the oxygen has to diffuse under the surface of the platinum grains to give a stable voltage and that it also diffuses to a similar depth below the ceramic surface at the same time. According to the observed pre-exponential factor, the depth of the reservoir should be $10^{-5.8 \pm 1.4} \text{ cm}$ (0.0200 ± 0.0006 microns).

At higher temperatures, the order decreased. The diffusion of holes or the reaction of holes with oxide anions could be the rate-limiting step. The first possibility is not preferred as the activation energy obtained in our experiment does not match with the activation energy for the diffusion of holes which is smaller as compared to the activation energy for a charge-transfer process. Heyne and Beekmans⁶⁸ observed an activation energy of 120 kJ mol^{-1} for the diffusion of electron holes in calcia-stabilized zirconia. Park and Blumenthal⁷⁵ observed an activation energy of 111 kJ mol^{-1} for the diffusion of holes in yttria-stabilized zirconia. So on the basis of the activation energy, the diffusion of holes as a rate limiting step at higher temperatures can be ruled out. Therefore reaction [4] could be the rate limiting step at higher temperatures.

So based on the rate equations and Arrhenius parameters, step [5] is considered to be rate limiting at 773 K for low surface coverage. It explains all the observed results. But the other mechanisms are possible too. At higher surface coverage, the later steps

in the mechanism could be rate limiting as adsorbed oxygen can have a concentration proportional to $P_{O_2}^{1/4}$ over a limited pressure range. But the surface coverage should decrease with increase in temperatures, so the order will show a greater dependence on pressure, so it should increase with rise in temperature. This is contrary to our experimental observations. So the diffusion of oxygen on the surface cannot be a rate limiting step.

These results suggest that for a fast response, the iron concentration in the electrolyte should be very small to minimize the oxygen uptake and small grains of platinum should be used to minimize the diffusion distance and reservoir depths.

The sensor became slow with aging. The response time of the sensor increased but the relative trends in response times on changing the pressure or temperature were not affected by aging.

4.2 Sensor B

4.2.1 Experimental Observations

The following observations were made in the Result section for sensor B:

1. Independence of $t_{1/2}$ on the partial pressure of oxygen
2. The shapes of the traces of voltage as a function of time
3. Dependence of R_i on the partial pressure of oxygen
4. Temperature dependence of R_i

5. Temperature dependence of R_b
6. Temperature dependence of response time
7. Increase of the interfacial resistance with time (aging)
8. Comparison of RC time constant and $t_{0.63}$
9. Independence of capacitance on temperature or aging
10. Angle of depression for the electrode semicircle

4.2.2 Earlier Work

Sasaki et al.⁵⁰ observed that the interfacial resistance for Pt electrodes on yttria-stabilized zirconia was proportional to $P_{O_2}^{-1/4}$ and that the interfacial capacitance and the angle of depression were independent of pressure and temperature. Wang and Nowick⁶⁰ observed that for platinum paste electrodes on yttria-stabilized ceria electrolyte, the exchange current I_0 was proportional to $P_{O_2}^{-1/4}$ at 773 K but showed a dependence on $P_{O_2}^{-1/4}$ at temperatures above 873 K. Using the impedance technique for Pt electrodes on ceria electrolyte at high temperatures and at high P_{O_2} they observed an angle of depression of 25 degrees and capacitance of 14.5 μ F. Bauerle⁴³ observed that for Pt electrodes on yttria-stabilized zirconia, the electrode resistance was proportional to $P_{O_2}^{-0.64}$ and the electrode capacitance was independent of temperature, pressure and electrode thickness. Chu and Seitz⁵¹ found that for Au and Pt electrodes on yttria-stabilized zirconia the electrode capacitance was dependent on temperature, electrode material and pressure of

oxygen, increasing with rise in temperature. Verkerk et al.⁴⁹ found that for Pt electrodes on yttria-stabilized zirconia, the electrode resistance at the anode varied as $P_{O_2}^{1/4}$ and that at the cathode as $P_{O_2}^{-1/4}$.

4.2.3 Response of the freshly prepared sensor

When freshly prepared, sensor B showed a very fast response. At 773 K, the values of $t_{1/4}$ and $t_{0.63}$ were 0.063 and 0.090 seconds, respectively. Fig. 3.2.1 is a trace of sensor output voltage as a function of time at 773 K. This sensor was faster than the commercial sensors produced by Honda and Bosch by about an order of magnitude and gave a satisfactory response down to 623 K as shown in Fig. 4.3.⁷⁶ Young and Bode⁷⁷ and Fleming et al.⁷⁸ observed that the time for a 90% EMF change was about 50 ms in combustion gases, but in that case a different mechanism may apply. Table 4.5 shows the values of $t_{0.63}$ obtained from the vacuum technique and the $R_i C_i$ obtained from the impedance technique at several temperatures.

4.2.4 A model for the behaviour of sensor B

For sensor B, it was observed that the response time was independent of the partial pressure of oxygen from 623 K to 855 K and that the interfacial resistance R_i showed a dependence on the inverse approximately quarter power of the partial pressure of oxygen at 773 K and 823 K. The various elementary steps for the overall reaction

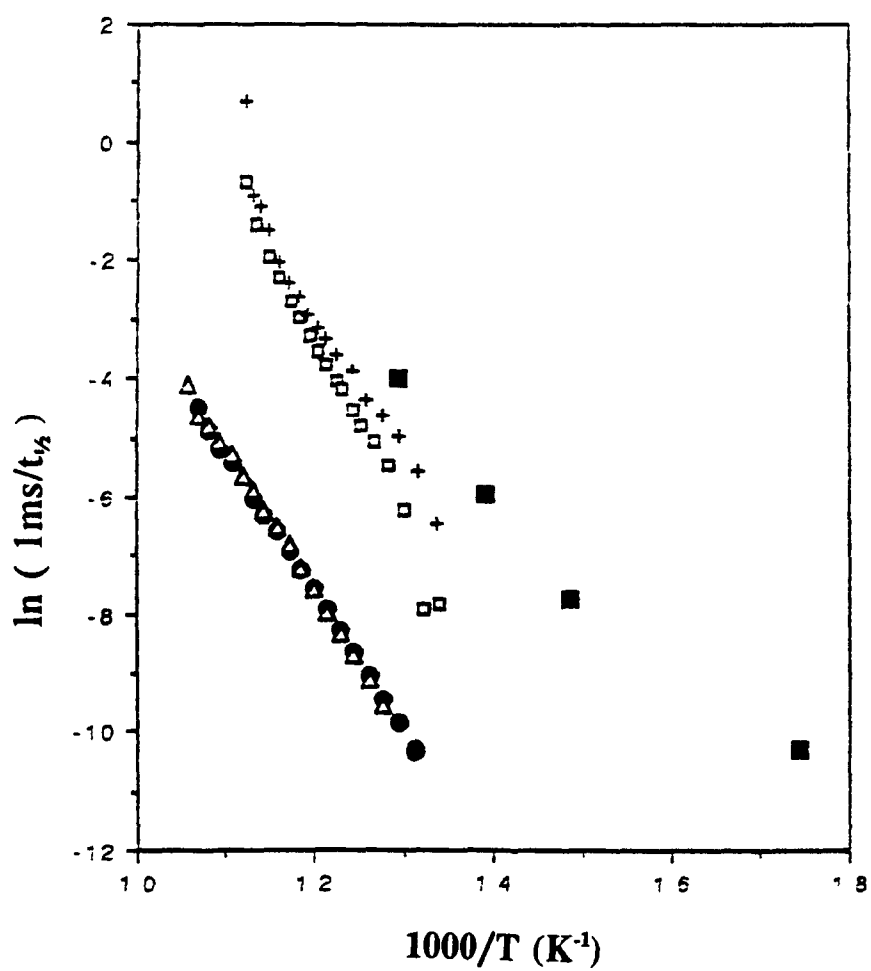


Fig. 4.3 Comparison of some sensors ■ sensor B; □ Bosch; Δ, ● Standard Motor products; + Honda.

Table 4.5 The values of $t_{0.63}$ and $R_i C_i$ at various temperatures.

T (K)	$t_{0.63}$ (s)	$R_i C_i$ (s)
773	0.09	-
673	3.75	-
723	0.46	-
823	0.08	0.08
860	0.09	0.064
773	0.68	0.64
823	0.23	0.27
855	-	0.106
823	0.54	0.60
673	59	63

* The values are reported in chronological order

would be the same as for sensor A. On the basis of the relationship between the capacity, response time and the rate of filling or emptying of the reservoir, some of the possibilities for a reaction to be the rate-limiting step can be eliminated. As the resistance is inversely proportional to the rate of the reaction, so the rate of the elementary reaction which could limit the response should show a quarter power dependence on the partial pressure of oxygen. From the dependence of $t_{1/2}$ and R_i on pressure, with holes as a principal reservoir, reactions [3] or [4] have the right order. This would be either the diffusion of holes from the bulk to the electrochemical reaction site or the reaction of oxide anions with the electron holes to form singly-charged oxygen anions. The expressions for the change of voltage with time, with various reservoirs and various elementary reactions rate-limiting, have been derived in section 4.1. If we consider reaction [3] or [4] to be rate-limiting, then the expression for the change of voltage with time will be given by the following general equation,

$$\Delta E = \frac{RT}{nF} \ln [A + (1-A)e^{-Bt}] \quad 4.75$$

$$\text{In this eq., } A = (P_f/P_i)^x \quad 4.76$$

where P_f and P_i are the final and initial pressures of the experiment and $x = 1/4$. The number n in the denominator is $4x$.

The exponential parameter B is given by,

$$B = v_{r,i} \phi_{i,j} [r]_{\infty} \quad 4.77$$

B for elementary reaction [3] will be,

$$B = k_3 [h]_{\infty} / [h]_{\infty} = k_3 \quad 4.78$$

B for reaction [4] will be,

$$B = k_4 [O^2(ERS)] [h]_{\infty} / [h]_{\infty} = k_4 [O^2(ERS)] \quad 4.79$$

The value of $t_{1/2}$ can be written as,

$$t_{1/2} = \frac{1}{B} \ln \left[\frac{1-A}{A^{1/2}-A} \right] \quad 4.80$$

Similarly, the value of $t_{0.63}$ would be,

$$t_{0.63} = \frac{1}{B} \ln \left[\frac{1-A}{A^{0.63}-A} \right] \quad 4.81$$

For different pressure ratios used in the experiment, $t_{0.63}$ equals 1.4 $t_{1/2}$.

The above equations explain the various observations for sensor B.

1. The response time was independent of the partial pressure of oxygen as $t_{1/2}$ and $t_{0.63}$ depend on parameter B, which does not depend on the partial pressure of oxygen for reaction [3] or [4]. $t_{1/2}$ or $t_{0.63}$ depend on the pressure through the logarithmic factor but this factor is too weak to be significant.

2. Eq. 4.75 was fitted to the experimental traces of voltage vs. time at several temperatures. The values of P_f and P_i were taken from the experimental data and the value of parameter B was determined using non-linear least squares.⁶⁷ The values and the SRMSD are given in Table 4.6. The values of $t_{1/2}$ and $t_{0.63}$ were calculated using eqs. 4.80 and 4.81, and match very well with the experimental values as shown in Table 4.7. This indicates that reaction [3] or [4] could be rate limiting.

Table 4.6 Results of non-linear least squares fits of eq. 4.75 to experimental traces of voltage vs time at some temperatures

T (K)	P_i(torr)	P_r(torr)	B (s⁻¹)	SRMSD (mV)
773	749	48.2	10.89 ± 0.56	1.8
718	761	48.7	2.25 ± 0.11	1.7
673	761	49.5	0.384 ± 0.04	3.6
623	755	49.4	0.033 ± 0.001	1.7
828	764	48.7	13.26 ± 1.7	3.6

Table 4.7 Comparison of response times obtained experimentally and calculated using eqs. 4.80 and 4.81

T	P_i	P_f	t_{0.63}	t_{0.63}	t_{1/2}	t_{1/2}
K	torr	torr	calc, s	expt, s	calc, s	expt, s
773	749	48.2	0.113	0.091	0.081	0.063
718	761	48.7	0.55	0.42	0.39	0.40
673	761	49.5	3.19	3.67	2.29	2.3
623	755	49.4	37.1	38.3	27.3	25
828	764	48.7	0.09	0.08	0.066	0.05

4.2.5 The Resistance and Capacitance for Sensor B

The electrode capacitance, C_i , is given by,

$$dQ_i = C_i dV \quad 4.82$$

where V is the potential applied at the electrode/electrolyte interface, and Q_i is the charge in the effective capacitor.

Since the concentration of electron holes represents a concentration of charges, dQ can be written in terms of $d[h]$ as,

$$dQ_i = F v d[h] \quad 4.83$$

where F is Faraday's constant and v is the volume occupied by the holes.

The Nernst equation in terms of electron holes is given by eq. 4.52 and can be written as,

$$\frac{[h]}{[h]_o} = e^{\frac{nFE}{RT}} \quad 4.84$$

On differentiating eq.4.84 we obtain,

$$d[h] = \frac{[h]_o nF}{RT} e^{\frac{nFE}{RT}} dE \quad 4.85$$

Substituting this in eq.4.83,

$$dQ_i = \frac{n F^2 v [h]_o}{RT} e^{\frac{nFE}{RT}} dE \quad 4.86$$

For small voltage changes, $e^{nFE/RT}$ will be 1. By comparison with eq.4.82, the capacitance

can be written as,

$$C_i = \frac{n F^2 v [h]_o}{RT} \quad 4.87$$

The volume v can be written as the product of the area, A , of the electrode/electrolyte interface and the depth, r_i , through which the holes have to diffuse in order to react at the ERS. Substituting the value of the concentration of holes in the steady state from eq. 4.2, we obtain,

$$C_i = \frac{n F^2 A r_i K_1^{1/4} P_{O_2}^{1/4} [Fe_z']}{R T} \quad 4.88$$

This gives an expression for the interfacial capacitance. The value of capacitance observed experimentally at 773 K at 1 atm pressure was approximately 10×10^{-6} F. The value of K_1 at the same pressure was calculated from the values of ΔS_1 and ΔH_1 from ref(37) and came out to be 4.56. The concentration of Fe in our sample was 3.0×10^{-6} mol cm^{-3} as reported earlier. The total contact area (area of the breaks in Fig 3.4.2) of the electrode/electrolyte interface was measured from SEM pictures to be approximately 0.00254 cm^2 for sensor A. Substituting these values at 773 K in eq. 4.88, the value of r_i came out to be 2.9 microns. This matches with the size of a Pt grain. Similar calculations were done at 673 K and 823 K and gave the value of r_i to be 1.3 and 5.3 microns, respectively. The response of sensor B was very fast compared to sensor A, so if we assume that for sensor B the number of contacts between the electrode and electrolyte were more than the above value for sensor A, then the value of the area A ,

would increase, which would give a lower value of r_i for the same capacitance. Then r_i would approach the radius of the electrode/electrolyte contact. The total electrode area for sensor B was measured to be approximately 0.95 cm^2 . If we substitute this value for the area A in eq. 4.88, then the value of r_i comes out to be 0.004 to 0.014 microns which is very small as compared to the size of the Pt grains, the radius of the electrode/electrolyte contact or the distance between the contacts.

The molar conductivity λ is related to the diffusion coefficient D of the species through the Nernst Einstein relation as,⁷⁰

$$D = \frac{R T \lambda}{n F^2} \quad 4.89$$

Here n is the number of charges per ion, λ is the molar conductivity in the units of $\text{ohms}^{-1} \text{ cm}^2 \text{ mol}^{-1}$, D is the diffusion coefficient in the units of $\text{cm}^2 \text{ s}^{-1}$. The resistance in ohms is related to the conductivity as,

$$R = \frac{l}{c \lambda A} \quad 4.90$$

where c is the concentration of the species in moles cm^{-3} , A is the cross-sectional area and l is the distance through which the charged species move. Therefore the resistance at the electrode/electrolyte interface can be related to the diffusion coefficient as,

$$R_i = \frac{R T l}{D_h n F^2 [h]_o A} \quad 4.91$$

Substituting the value of the concentration of holes in the steady state from eq.4.2, we get

$$R_i = \frac{R T l}{D_h n F^2 K_1^{1/4} P_{O_2}^{1/4} [Fe_z'] A} \quad 4.92$$

The value of D_h was found to be $1.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for calcia-stabilized zirconia from ref (79) by extrapolation to 773 K. The value of the iron concentration in that sample was 6 times the concentration in our sample and the diffusion coefficient of holes is inversely proportional to the concentration of Fe.³⁷ The experimental value of R_i was 5.05×10^5 ohms at 773 K. If the adjustment for the Fe concentration is made, then on substituting all the other values in the above equation, the value of l comes out to be 11 microns which is approximately equal to the distance between the electrode/electrolyte contacts. Park and Blumenthal⁷⁵ gave an empirical equation for the diffusion coefficient of holes in 8 mole percent yttria-stabilized zirconia. The iron concentration in their sample was not reported but was presumably higher than in our sample as the concentration of other impurities was higher too. Substituting their value of diffusion coefficient, $D_h = 7.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, the value of l came out to be 1.44 microns which is the size of a contact between electrode and electrolyte. As suggested above, the electrode/electrolyte contact area would be greater for sensor B, which would again make the value of l smaller.

Similar calculations were done at 673 and 823 K. Using the diffusion coefficient from ref (79) with the adjusted value for Fe concentration, gave the value of l to be 24 microns and 1.4 microns, respectively. If A is taken to be the area of the electrode, then l comes out to be 0.91 to 0.05 cm which is very large compared to the size of a Pt grain or the distance between the Pt grains or the radius of the electrode/electrolyte contacts.

The combination of eqs. 4.88 and 4.92 will give $R_i C_i$, as

$$R_i C_i = \frac{l r_i}{D_h} \quad 4.93$$

Since RC is observed to be equal to $t_{0.63}$ experimentally, so according to this equation, the response time will depend on the concentration of Fe through the diffusion coefficient of electron holes and on the morphology of the electrodes through l and r_i .

4.2.6 Arrhenius parameters

Now we will find Arrhenius parameters for σ_i and G_i , where G_i is the interfacial conductance. Differentiating eq.4.88 with respect to temperature will give,

$$R \frac{d \ln C_i}{d(1/T)} = \frac{R}{4} \frac{d \ln K_1}{d(1/T)} - R \frac{d \ln T}{d(1/T)} \quad 4.94$$

This can be written in terms of activation energy as,

$$E_{AC_i} = \frac{\Delta H_1}{4} - RT \quad 4.95$$

where E_{AC_i} is the activation energy for capacitance.

Differentiating eq.4.92 for the resistance with respect to temperature, we get,

$$R \frac{d \ln R_i}{d(1/T)} = -\frac{R}{4} \frac{d \ln K_1}{d(1/T)} + R \frac{d \ln T}{d(1/T)} - R \frac{d \ln D_h}{d(1/T)} \quad 4.96$$

The activation energy will be,

$$E_{AR_i} = -E_{AD_h} - \frac{\Delta H_1}{4} + RT \quad 4.97$$

where E_{AR_i} is the activation energy for the conductance and E_{AD_h} is the activation energy for the diffusion of holes.

Heyne and Beekmans⁶⁸ observed an activation energy for diffusion of holes in calcia-stabilized zirconia of 120 kJ mol⁻¹. Park and Blumenthal⁷⁵ observed an activation energy of 111 kJ mol⁻¹ for the diffusion of holes in yttria-stabilized zirconia. Dou et al.⁷³ observed an activation energy of 88 ± 13 kJ mol⁻¹ for the diffusion of holes in calcia-stabilized zirconia. Weppner^{80,81} observed an activation energy of 135 kJ mol⁻¹ for the diffusion of holes in yttria-stabilized zirconia. The value of ΔH_1 for calcia-stabilized zirconia was 148 ± 53 kJ mol⁻¹.³⁷ Substituting these values in eq. 4.95 and eq. 4.97, the activation energy for capacitance at 773 K was determined to be 37 ± 13 kJ mol⁻¹ and the activation energy for conductance was calculated as 151 ± 13 kJ mol⁻¹,⁶⁸ 142 ± 13 kJ mol⁻¹,⁷⁵ 119 ± 26 kJ mol⁻¹,⁷³ and 165 ± 13 kJ mol⁻¹,^{80,81} respectively. These match

with the activation energy of $119 \pm 17 \text{ kJ mol}^{-1}$ for the interfacial conductance observed experimentally. The low activation energy for the capacitance suggests that it would not show a significant dependence on temperature and this is in accordance with our experimental observations. Other authors also found the electrode capacitance to be independent of temperature.^{43,49,50} The close agreement for the activation energy for the conductance suggests that the diffusion of holes is the rate-determining step. The activation energy for RC would be a combination of the two activation energies which will come out to be 188 ± 26 ,⁶⁸ 179 ± 26 ,⁷⁵ 156 ± 39 ,⁷³ and 202 ± 26 ,^{80,81} kJ mol^{-1} which matches with the activation energy of $145 \pm 14 \text{ kJ mol}^{-1}$ obtained for the response time.

Now we have to eliminate the possibility of some other reaction being rate limiting.

The diffusion of oxide anions in the bulk could be considered rate limiting as the response time does not show any dependence on the partial pressure of oxygen. But the process in the bulk had a lower activation energy as compared to the process occurring on the interface between the platinum and stabilized zirconia. The activation energy for the conductance due to the bulk was found to be $80 \pm 17 \text{ kJ mol}^{-1}$ which matches with the activation energy of 75 ,¹ 71 ,⁸² 77 ,⁸³ kJ mol^{-1} for the diffusion of the oxide anions in yttria-stabilized zirconia. So this cannot be the rate limiting step.

Mass transport processes in the gas phase can be eliminated because at all the temperatures the RC time constants obtained from the impedance technique were equal to $t_{0.63}$ obtained from the vacuum technique. So the response of the sensor corresponded

to the electrode/electrolyte interface and did not depend on the diffusion of the gas through the solenoid. Also the time required for the pressure to reach 90% of its final value was 25 ms.

4.2.7 Depression of the semicircle

As shown in Table 3.3.3, the angle of depression of the semicircle was 31 ± 1 degrees and this did not show any dependence on temperature or pressure. A similar value has been observed by other authors 25 deg⁴⁵, 10-20 deg⁴⁹, 30 deg⁵⁰. Wang and Nowick⁴⁵ proposed that the large value of the angle of depression could be due to the distribution of the circuit parameters. According to McDonald and Johnson⁴⁴, the semicircle is depressed because of the distributed elements in the material electrode system. Then the RC time constant or the relaxation time τ is not single-valued but is distributed around a mean value. The angle of depression is related to the width of the relaxation time distribution. Due to the roughness of the surface, the contributions from the reaction resistance and capacitance differ with the electrode position and vary over a certain range around a mean, and only the average effect over the entire electrode is observed.

Recently a model was proposed⁸⁴ in which the electrode surface consists of a ladder network of elements, each consisting of a parallel combination of capacitance and charge transfer resistance. The depression of the semicircular arc depended on the standard deviation of the normal distribution of the double layer capacitance. Due to the heterogenous nature of the surface at the microscopic level, there is an uneven charging

of the double layer, which leads to distribution of the values of interfacial capacitance and charge transfer resistance. In their model they assumed that the charge transfer resistance stayed the same whereas the range of the value of capacitance depended on the angle of depression. So if the value of capacitance is distributed, it should be due to a range of values of the electrode/electrolyte contact area. As measured from the scanning electron micrographs, the mean size of the electrode/electrolyte contact was 0.91 ± 0.38 microns. It can be seen that the standard deviation is very large and according to this model would give a large angle of depression.

4.3 Comparison between sensor A and sensor B:

For sensor A, the response time showed a negative quarter power dependence on the partial pressure of oxygen at 773 K and the activation energy obtained was 210 kJ/mol. For sensor B, the response time did not show any dependence on the partial pressure of oxygen and the activation energy was 145 ± 14 kJ/mol. Because of the difference in the oxygen pressure dependence and the activation energies of the response times of the two sensors A and B, the rate determining steps were different. As seen in the SEM pictures of sensor A, a very small area of the electrode is in contact with the surface of zirconia. For sensor B, a platinum gauze was tightly pressed on to the platinum paste on zirconia. This force of the gauze resulted in increasing the number of contacts between the grains of the electrode and the electrolyte. So the total area of the contacts between the electrode and electrolyte increased. From the pictures obtained on

the optical microscope for sensor A, it can be seen that the platinum paste is not present continuously and homogeneously on the surface of zirconia but forms small patches. It may be possible that sometimes there is no contact between the various patches. When the platinum gauze is pressed on to the platinum paste, then these various isolated patches make a contact with each other through the wires in the gauze thereby increasing the total area of contact between the electrode and the electrolyte.

Sensor B showed a slower response with aging. The resistance of the sensor increased significantly due to aging but the capacitance stayed the same. The capacitance is related to the area of contact between the electrode and electrolyte.⁵⁰ Since the capacitance stayed the same after the aging of the sensor, the contact area was the same. The resistance did increase with aging. Since R is proportional to l/A , the increase in the value of the resistance would be due to the increase in the distance l that the holes have to travel to reach the ERS. Due to heating the sensor for a long period of time, grain growth may have occurred in the platinum thus increasing the size of the grains. Due to the grain growth, the distance between the centres of the grains will also increase. Some of the electrode/electrolyte contacts could also be removed with time but as the capacitance stayed the same, so A will stay the same. Verkerk et al.²⁴ observed that the electrode resistance increased with the size of the platinum particle and suggested that, with increasing particle size, the electrode/electrolyte contact area remained nearly constant. According to this argument, l should be either the length of the grain or the distance between the grains. The response time of the sensor would also increase as the response time is directly proportional to the resistance. The parameter B is proportional

to $1/t_{0.63}$, and $t_{0.63}$ has been observed to be equal to $R_i C_i$, which should be given by,

$$R_i C_i = \frac{l r_i}{D_h}$$

Since the diffusion coefficient of holes would stay the same after aging, increase in l or r_i would increase the value of the response time. If l is assumed to be the size of the platinum grain then due to the increase in size of the Pt grain, R_i will increase.

4.4 Conclusion

Two oxygen sensors, A and B, employing yttria-stabilized zirconia as an electrolyte, were prepared using the slip-casting technique. The two sensors differed in the construction of their electrodes. For sensor A, platinum paste was used for the electrodes and for sensor B, in addition, platinum gauze was pressed onto the inner electrode. Three techniques were used to study the mechanism of oxygen transfer reactions on the surface of the sensors. These techniques were response time measurements, the impedance technique and scanning electron microscopy.

Sensor A

1. By exposing the sensor to rapid changes in the partial pressure of oxygen, EMF vs time plots were obtained from which the response times were calculated. Two kinds of experiments were performed. When the pressure on the inside of the sensor changed

from low to high, the response was faster than in experiments in which the pressure in contact with the sensor changed from high to low.

2. The response time of the sensor was studied as function of the partial pressure of oxygen at 773 K, 823 K, 873 K and 923 K for the p-drop experiments. At 773 K, the response time showed an inverse quarter-power dependence on the partial pressure of oxygen. At higher temperatures, the order decreased, approaching zero as shown in Table 3.1.7 and Figs. 3.1.4 to 3.1.6. The response time showed an opposite dependence on pressure for p-jump experiments at 773 K.

3. The response times were studied as a function of the bulb size B' . Changing the size of the bulb changed the ratio P_i/P_f . A smaller P_i/P_f ratio gave a faster response. This was due to the greater value of P_f .

4. The Arrhenius plots of inverse of response time with respect to inverse temperature gave an activation energy of $210 \pm 14 \text{ kJ mol}^{-1}$ and a pre-exponential factor of $10^{12.8 \pm 0.9} \text{ s}^{-1}$.

5. The differential rate equations for the various possible elementary steps were integrated and it was found that all elementary processes could be described by one of two general equations, eq. 4.54 and eq. 4.55. Rearrangement of these equations gave

expressions for the calculation of response times according to eqs. 4.61 and 4.65. Eq. 4.55 explained all the experimental observations at 773 K. The inverse dependence on the quarter power of the partial pressure of oxygen was due to the presence of an $[h(\text{ERS})]$ factor in the exponential in eq. 4.55. Eq. 4.55 was fitted to the experimental traces of voltage vs time at 773 K as shown in Figs. 4.1 and 4.2. The value of response time was inversely proportional to the parameter B obtained from the curve fit. The results were consistent with a mechanism in which reaction [5] (conversion of electron holes and singly charged oxygen anions to neutral oxygen atoms at the surface of zirconia) was considered to be rate limiting at 773 K as it gave the right order and Arrhenius parameters. The activation energy for the diffusion of oxygen atoms on the surface of platinum is 142 kJ mol^{-1} .⁸⁵ The heat of adsorption of oxygen on the surface of platinum is -71 kJ mol^{-1} .⁶² These two values would give an activation energy of 106 kJ mol^{-1} which is very small compared to our experimental value of $210 \pm 14 \text{ kJ mol}^{-1}$. So the diffusion of oxygen on the surface of platinum, step [6], can be ruled out as a rate limiting.

6. At higher temperatures, the order of the response time with respect to the partial pressure of oxygen approached zero. Eq. 4.54 was fitted to the experimental traces of voltage vs time and there was a good agreement between the theoretical and experimental values. The response times were calculated using eq. 4.65 with the values of the parameter B obtained from the fit. There was a good match between the theoretical and experimental values. Based on these observations, reaction [3] or [4] could be the rate-

limiting step at higher temperatures.

It was concluded that for a fast response, one should keep the iron concentration to a minimum and size of the Pt grains small.

Sensor B

1. Sensor B was observed to be more than two orders of magnitude faster than sensor A. Sensor B showed a faster response than some commercial sensors.

2. The order of the response time with respect to the partial pressure of oxygen was observed to be about zero at 623 K to 823 K as shown in Table 3.2.7 and Fig. 3.2.2.

3. The variation of response times with respect to the inverse temperature (Fig. 3.2.3) gave an activation energy of $145 \pm 14 \text{ kJ mol}^{-1}$ and a pre-exponential factor of $10^{9.7 \pm 1.2}$. Based on the order and the Arrhenius parameters, reaction [3], the diffusion of electron holes, was considered to be rate limiting. Fitting eq. 4.54 to the experimental traces of voltage vs time gave the value of the parameter B. The values of $t_{1/2}$ and $t_{0.63}$ were calculated using eqs. 4.80 and 4.81 and were found to be in agreement with the experimental value as shown in Table 4.6.

4. Using the impedance technique, the values of the resistance due to the bulk of the electrolyte, R_b , the interfacial resistance, R_i , the bulk capacitance, C_b and the interfacial

capacitance C_i were obtained. The interfacial resistance decreased with a rise in temperature; the energy of activation was $119 \pm 17 \text{ kJ mol}^{-1}$ and the pre-exponential factor was $10^{-2.6 \pm 1.2}$. The interfacial capacitance stayed almost the same with changes in the partial pressure of oxygen or temperature.

The resistance due to the bulk, R_b , decreased with increase in temperature and the activation energy obtained for this process was $80 \pm 17 \text{ kJ mol}^{-1}$ and the pre-exponential factor was $10^{-2.6 \pm 1.2}$. The capacitance due to the bulk did not show any dependence on the pressure or temperature. From a theoretical expression obtained for interfacial capacitance, a small activation energy of 37 kJ mol^{-1} was obtained. From the expression for the interfacial resistance, R_i , the activation energy obtained was in agreement with the experimental value.

5. The response time, $t_{0.63}$, obtained from the vacuum technique was observed to be equal to the $R_i C_i$ constant from the impedance technique.

6. From the expressions for R_i and C_i , $R_i C_i$ was found to be equal to $l r_i / D_h$. So the response time shows an inverse dependence on the concentration of Fe through the diffusion coefficient of holes, and shows a direct dependence on the radius of the electrode/electrolyte contacts and the length l . " l " could be the size of the platinum grains or the distance between the various grains.

APPENDIX

Table 5.1 Real and imaginary parts of the impedance from the measurements on the gain phase meter at 773 K. The value of R_s was 100 k Ω .

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z"(ohms)
5.0	-27.4	-31.8	3705.5	2419.0
6.0	-28.0	-32.5	3423.6	2289.1
7.0	-28.5	-33.0	3208.6	2181.3
8.0	-28.9	-33.3	3050.2	2093.4
9.0	-29.3	-33.6	2899.8	2009.3
10.0	-29.6	-33.8	2792.7	1947.0
15.0	-31.0	-34.3	2356.7	1664.4
20.0	-32.0	-33.8	2111.1	1457.2
30.0	-33.2	-34.0	1831.4	1268.8
40.0	-34.2	-33.6	1638.7	1114.8
50.0	-34.9	-33.1	1519.9	1012.5
70.0	-36.0	-32.2	1351.9	867.6
90.0	-36.7	-31.5	1256.4	783.4
100.0	-37.1	-31.2	1203.4	740.9
200.0	-39.1	-29.4	972.7	555.2
300.0	-40.3	-28.5	854.1	468.9
400.0	-41.0	-28.0	791.4	425.1
500.0	-41.6	-27.5	741.8	389.8
700.0	-42.3	-26.7	689.1	349.6
900.0	-42.9	-26.1	646.3	319.1
1000.0	-43.2	-25.9	625.3	306.0
1500.0	-44.3	-24.5	557.1	255.6
2000.0	-44.9	-23.5	523.9	229.2
3000.0	-45.9	-21.9	472.3	190.9
5000.0	-46.9	-19.9	426.5	155.1
7000.0	-47.5	-18.4	401.6	134.2
9000.0	-48.0	-17.3	381.4	119.3
10000.0	-48.1	-16.9	377.8	115.3
20000.0	-48.8	-13.6	354.1	86.0
30000.0	-49.2	-11.8	340.5	71.4
50000.0	-49.7	-9.4	324.0	53.8
70000.0	-50.0	-7.9	314.2	43.7
90000.0	-50.1	-6.6	311.5	36.2
100000.0	-50.2	-6.0	308.3	32.5
200000.0	-50.7	-1.9	292.4	9.7

Table 5.2 Real and imaginary parts of the impedance from the measurements on the gain phase meter at 673 K. R_s was 100 k Ω for this experiment.

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
4.0	-10.7	-30.6	28477.4	25477.3
5.0	-11.0	-33.3	25666.8	25436.7
6.0	-11.4	-33.0	24685.6	23605.7
7.0	-12.0	-32.9	23047.3	21274.5
8.0	-12.4	-33.3	21773.6	20059.3
9.0	-12.7	-33.8	20771.8	19282.0
10.0	-13.2	-32.7	20044.4	17389.1
15.0	-14.6	-35.3	16053.0	14726.1
20.0	-15.4	-35.9	14425.7	13211.9
30.0	-17.1	-35.9	11801.2	10321.6
40.0	-18.2	-35.7	10397.3	8805.5
50.0	-19.0	-35.3	9522.8	7817.2
60.0	-19.3	-36.5	9000.8	7698.9
70.0	-20.1	-34.8	8426.1	6657.9
80.0	-20.6	-34.5	7977.6	6183.3
90.0	-21.1	-34.2	7552.9	5744.8
100.0	-21.4	-34.0	7310.6	5495.3
150.0	-22.8	-32.6	6316.2	4419.2
200.0	-23.7	-31.6	5751.8	3832.4
300.0	-25.0	-29.9	5033.4	3095.1
400.0	-25.8	-28.6	4646.0	2690.3
500.0	-26.4	-27.5	4378.2	2409.0
600.0	-26.9	-26.5	4168.4	2188.9
700.0	-27.3	-25.6	4010.1	2017.7
800.0	-27.6	-24.8	3898.8	1888.1
900.0	-27.9	-24.1	3786.2	1771.8
1000.0	-28.1	-23.5	3716.7	1688.5
1500.0	-28.9	-21.1	3446.2	1382.9
2000.0	-29.4	-19.5	3285.3	1206.8
3000.0	-30.0	-17.5	3099.9	1010.9
4000.0	-30.3	-16.2	3014.2	904.5
5000.0	-30.6	-15.4	2921.9	830.3
6000.0	-30.8	-14.8	2862.3	779.5

Contd..

8000.0	-31.1	-14.1	2772.2	716.9
10000.0	-31.3	-13.7	2712.6	680.3
20000.0	-31.9	-13.6	2528.5	628.2
30000.0	-32.2	-14.6	2429.1	649.2
40000.0	-32.5	-15.9	2329.3	680.4
50000.0	-32.8	-17.4	2229.8	715.9
60000.0	-33.0	-19.0	2156.8	760.7
70000.0	-33.1	-20.5	2110.4	808.2
80000.0	-33.3	-22.0	2039.3	843.7
90000.0	-33.6	-23.4	1947.6	862.5
100000.0	-33.7	-24.9	1901.2	903.0
200000.0	-36.0	-34.8	1310.1	928.5
300000.0	-38.0	-38.0	995.8	790.6
400000.0	-39.6	-37.2	837.0	643.8
500000.0	-40.8	-34.6	753.6	525.8
600000.0	-41.6	-31.1	715.4	435.8
700000.0	-42.0	-28.1	704.2	379.4
800000.0	-42.1	-24.6	718.0	331.6
900000.0	-42.3	-22.5	713.1	297.9
1000000.0	-42.4	-20.4	715.4	268.2
1500000.0	-42.7	-14.4	714.5	184.9
2000000.0	-42.7	-12.9	719.2	166.0

Table 5.3 Real and imaginary parts of the impedance from the measurements with the gain phase meter at 723 K. R_s was 100 k Ω for this experiment.

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z"(ohms)
1.0	-13.7	-27.3	20851.9	14022.4
1.5	-14.8	-29.8	17396.8	12606.8
2.0	-15.6	-30.3	15621.1	11300.0
3.0	-16.8	-32.9	12910.5	10088.9
4.0	-17.4	-35.2	11536.6	9747.1
5.0	-18.4	-35.3	10226.0	8491.3
6.0	-18.8	-35.2	9767.8	8016.7
7.0	-19.4	-35.2	9096.1	7384.8
8.0	-19.9	-35.6	8515.7	6963.2
9.0	-20.3	-35.8	8094.6	6627.7
10.0	-20.6	-36.3	7748.2	6437.5
15.0	-22.0	-36.5	6549.1	5377.9
20.0	-23.3	-35.0	5752.1	4394.4
30.0	-24.6	-36.4	4834.2	3845.7
40.0	-25.7	-36.1	4269.1	3326.6
50.0	-26.5	-35.8	3904.5	2990.6
60.0	-26.9	-34.4	3799.8	2752.3
70.0	-27.4	-35.3	3539.6	2644.4
80.0	-27.8	-35.1	3387.3	2505.3
90.0	-28.2	-34.9	3241.2	2373.8
100.0	-28.5	-34.7	3138.2	2277.0
150.0	-30.0	-33.9	2661.8	1859.5
200.0	-30.9	-33.3	2414.8	1642.2
300.0	-32.2	-32.2	2103.0	1364.0
400.0	-33.1	-31.4	1911.3	1197.7
500.0	-33.8	-30.7	1775.5	1079.9
600.0	-34.3	-30.0	1687.9	996.7
700.0	-34.7	-29.4	1621.3	933.3
800.0	-35.1	-28.9	1555.5	876.3
900.0	-35.5	-28.4	1492.2	822.6
1000.0	-35.7	-28.2	1460.8	798.1
1500.0	-36.8	-26.5	1306.2	662.0
2000.0	-37.5	-25.1	1219.1	579.6

3000.0	-38.5	-23.1	1103.0	476.5
4000.0	-39.1	-21.7	1039.6	418.7
5000.0	-39.6	-20.5	989.1	374.0
6000.0	-39.9	-19.4	962.2	342.5
7000.0	-40.1	-18.6	944.7	321.3
8000.0	-40.3	-17.9	926.9	302.5
9000.0	-40.4	-17.3	919.4	289.2
10000.0	-40.5	-16.8	911.3	277.8
20000.0	-41.4	-13.8	833.0	206.4
30000.0	-41.8	-12.4	799.9	177.2
40000.0	-42.2	-11.7	765.7	159.8
60000.0	-42.5	-10.8	741.9	142.6
80000.0	-42.8	-10.3	717.7	131.4
100000.0	-42.9	-10.2	709.7	128.6
150000.0	-43.3	-10.0	677.9	120.4
200000.0	-43.7	-9.7	647.9	111.5
300000.0	-44.0	-8.9	627.2	98.9
400000.0	-44.3	-7.3	608.2	78.4
500000.0	-44.5	-5.0	596.9	52.5
600000.0	-44.5	-3.2	598.3	33.7
700000.0	-44.5	-1.5	599.0	15.8
800000.0	-44.5	-0.4	599.2	4.2

Table 5.4 Real and imaginary parts of the impedance from the measurements with the gain phase meter at 623 K. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z"(ohms)
5.0	-17.4	-22.3	138715	66600
7.0	-17.8	-21.1	133463	59745
8.0	-18.2	-21.0	126966	56139
9.0	-18.3	-20.7	125719	54603
10.0	-18.6	-19.4	122471	49263
20.0	-19.6	-16.5	110390	36706
40.0	-21.3	-15.9	89559	28023
50.0	-21.2	-15.6	90853	27889
70.0	-21.9	-15.3	83442	24900
90.0	-22.2	-15.4	80357	24072
100.0	-22.2	-15.2	80453	23772
200.0	-23.6	-14.4	68038	18751
400.0	-24.1	-13.7	64245	16734
600.0	-24.7	-13.8	59687	15595
800.0	-25.2	-14.2	56057	15037
900.0	-25.5	-14.3	54031	14572
1000.0	-33.2	-14.7	21587	5795
2000.0	-33.8	-18.9	19651	6876
3000.0	-34.8	-22.2	17086	7113
4000.0	-35.4	-25.1	15565	7430
6000.0	-36.5	-31.5	12859	8021
8000.0	-37.4	-36.4	10910	8182
9000.0	-37.8	-39.0	10045	8272
10000.0	-38.1	-42.2	9233	8515
15000.0	-39.8	52.0	6274	8166
20000.0	-41.3	-60.2	4240	7535
30000.0	-44.2	-67.0	2383	5703
50000.0	-46.4	-73.8	1316	4608
60000.0	-37.2	-75.3	3335	13444
80000.0	-39.6	-77.0	2256	10250
90000.0	-40.6	-77.6	1924	9151

Contd..

100000.0	-41.6	-75.8	1979	8096
200000.0	-39.6	-73.6	2863	10104
300000.0	-42.9	-68.6	2575	6702
400000.0	-44.9	-63.6	2510	5121
600000.0	-47.0	-59.0	2291	3846
800000.0	-47.9	-48.5	2666	3032
1000000	-48.2	-43.9	2804	2713
1500000	-48.5	-39.2	2915	2389
2000000	-48.7	-58.8	1896	3153

Table 5.5 Real and imaginary parts of the impedance from the measurements with the gain phase meter at 823 K. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z''(ohms)
1.0	-44.0	-17.7	6043.3	1941.5
2.0	-45.2	-22.3	5106.1	2106.6
3.0	-46.1	-25.4	4491.0	2144.4
4.0	-46.9	-27.0	4038.0	2067.9
5.0	-47.4	-28.8	3747.8	2070.5
6.0	-48.0	-29.7	3466.2	1986.3
7.0	-48.4	-30.5	3282.8	1942.4
9.0	-49.3	-31.6	2924.8	1806.6
10.0	-49.6	-32.0	2812.9	1764.6
20.0	-52.1	-31.9	2110.9	1317.7
30.0	-53.6	-31.3	1787.2	1089.3
40.0	-54.5	-30.1	1631.4	947.8
60.0	-55.7	-27.1	1462.0	749.6
80.0	-56.4	-26.1	1360.6	667.7
100.0	-57.0	-24.8	1283.6	594.0
200.0	-58.3	-21.1	1135.8	438.8
300.0	-59.0	-19.4	1059.3	373.5
500.0	-59.9	-18.0	962.9	313.2
700.0	-60.4	-17.1	913.5	281.3
900.0	-60.8	-16.6	874.7	261.0
1000.0	-61.0	-15.7	858.7	241.6
2000.0	-61.9	-14.5	778.5	201.5
3000.0	-62.5	-13.7	729.1	177.8
5000.0	-63.0	-13.1	690.0	160.7
7000.0	-63.5	-12.6	652.6	146.0
9000.0	-63.7	-12.2	638.8	138.2
10000.0	-63.8	-12.0	631.9	134.4
20000.0	-64.5	-11.1	584.8	114.8
40000.0	-65.1	-10.2	547.4	98.5
60000.0	-65.4	-9.5	529.9	88.7
80000.0	-65.6	-8.8	518.9	80.4
100000.0	-65.4	-8.4	531.5	78.5
200000.0	-66.0	-2.9	500.8	25.4
300000.0	-66.4	-0.2	478.9	1.7

Table 5.6 Real and imaginary parts of the impedance from the measurements on the gain phase meter at 860 K. $R_s = 1 \text{ M}\Omega$

Freq (Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z''(ohms)
1.0	-16.9	-46.2	4706.1	1437.3
1.5	-19.5	-46.8	4324.9	1539.0
2.0	-22.0	-47.4	3968.3	1610.8
3.0	-25.3	-48.3	3486.3	1655.1
4.0	-27.8	-49.0	3145.7	1665.2
5.0	-29.5	-49.6	2887.7	1640.0
6.0	-30.7	-50.2	2661.8	1586.2
7.0	-31.6	-50.6	2517.6	1554.2
8.0	-32.4	-51.1	2355.6	1499.9
9.0	-33.1	-51.5	2231.8	1459.5
10.0	-33.6	-51.8	2143.6	1428.6
15.0	-35.3	-53.3	1766.7	1254.2
20.0	-35.4	-54.4	1554.4	1107.2
30.0	-35.7	-55.9	1302.8	938.0
40.0	-35.1	-57.0	1156.4	814.1
50.0	-34.4	-57.6	1088.4	746.4
60.0	-33.3	-58.3	1017.1	669.1
70.0	-33.0	-58.7	974.6	633.8
90.0	-31.5	-59.5	903.7	554.5
100.0	-30.9	-59.8	878.6	526.4
200.0	-26.7	-61.7	735.0	370.0
300.0	-24.6	-62.6	674.4	309.0
400.0	-23.1	-63.2	636.7	271.8
600.0	-21.6	-63.9	593.7	235.2
800.0	-20.5	-64.4	564.7	211.3
1000.0	-18.6	-64.8	545.6	183.7
2000.0	-16.7	-65.9	485.8	145.8
3000.0	-15.9	-66.5	455.2	129.8
4000.0	-15.2	-66.9	436.2	118.6
6000.0	-14.3	-67.4	413.5	105.5
8000.0	-13.5	-67.8	396.3	95.2
10000.0	-13.0	-68.0	388.0	89.6
15000.0	-12.0	-68.5	367.8	78.2

Contd..

20000.0	-11.3	-68.8	356.2	71.2
30000.0	-10.5	-69.1	345.0	64.0
50000.0	-9.1	-69.6	327.1	52.4
60000.0	-8.4	-69.7	323.9	47.8
80000.0	-7.6	-69.9	317.2	42.3
200000.0	-0.9	-70.3	305.5	4.8

Table 5.7 Components of the impedance at 823 K when the pressure on the inside of the sensor was 760 torr. $R_s = 1M\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z''(ohms)
1.0	-36.2	-31.4	13330	8286.4
2.0	-38.1	-36.8	10008	7605.0
3.0	-39.6	-40.4	7991.2	6896.0
5.0	-41.7	-44.0	5916.9	5779.6
7.0	-43.2	-46.2	4786.2	5041.3
10.0	-45.0	-47.7	3781.6	4190.8
20.0	-48.6	-52.4	2263.4	2957.0
30.0	-50.5	-51.9	1840.0	2357.9
50.0	-52.6	-52.4	1429.0	1862.6
70.0	-54.9	-52.2	1101.7	1424.5
80.0	-55.6	-52.0	1021.1	1310.5
90.0	-56.2	-51.7	959.3	1217.8
100.0	-56.8	-51.6	897.4	1134.8
200.0	-60.2	-48.8	643.6	736.3
400.0	-63.1	-44.8	496.6	493.6
600.0	-64.3	-40.8	461.5	398.7
800.0	-66.3	-38.3	380.0	300.3
1000.0	-67.0	-36.5	359.1	265.9
2000.0	-68.9	-31.2	307.1	186.0
4000.0	-70.3	-26.7	273.0	137.3
6000.0	-70.9	-24.6	259.3	118.7
8000.0	-71.1	-23.0	256.5	108.9
10000.0	-73.1	-22.7	204.2	85.4
20000.0	-73.7	-19.1	195.2	67.6
40000.0	-74.1	-15.6	190.0	53.1
60000.0	-74.4	-13.8	185.1	45.5
80000.0	-74.4	-12.6	186.0	41.6
100000.0	-74.7	-11.6	180.3	37.0

Table 5.8 Components of the impedance at 823 K when the pressure on the inside of the sensor was 316 torr. $R_s = 1\text{M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
1.0	-36.5	-31.0	12930.3	7906.9
2.0	-38.5	-36.8	9555.9	7256.2
3.0	-39.9	-39.5	7824.4	6536.1
4.0	-41.1	-41.4	6618.3	5904.1
5.0	-42.0	-43.4	5774.5	5521.0
7.0	-43.6	-45.5	4630.0	4756.3
8.0	-44.2	-46.3	4257.9	4495.9
10.0	-45.3	-47.4	3674.6	4028.3
20.0	-48.5	-52.4	2289.6	2991.4
40.0	-52.1	-51.6	1541.0	1952.0
60.0	-53.9	-49.5	1310.2	1538.7
80.0	-55.6	-51.1	1041.6	1294.3
100.0	-57.0	-51.1	886.6	1101.3
200.0	-60.3	-48.8	636.2	727.8
300.0	-62.2	-46.7	532.3	565.5
500.0	-64.5	-43.6	431.4	411.1
800.0	-66.4	-40.5	364.0	311.1
1000.0	-67.1	-36.3	355.9	261.6
2000.0	-69.1	-31.3	299.7	182.3
4000.0	-70.3	-26.6	273.2	136.9
6000.0	-72.2	-25.4	221.8	105.3
8000.0	-72.6	-23.8	214.5	94.6
10000.0	-73.0	-22.7	206.6	86.4
20000.0	-73.8	-19.0	193.1	66.5
40000.0	-74.2	-15.4	188.0	51.8
60000.0	-74.7	-13.7	178.9	43.6
80000.0	-74.6	-12.4	181.9	40.0
100000	-74.9	-11.6	176.2	36.2

Table 5.9 Components of the impedance at 823 K when the pressure on the inside of the sensor was 269 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
1.0	-37.6	-29.8	11526.9	6703.2
2.0	-39.6	-35.4	8571.1	6170.5
3.0	-41.0	-37.6	7081.4	5515.6
4.0	-42.1	-40.6	5971.3	5171.3
5.0	-43.0	-41.8	5283.0	4768.6
7.0	-44.5	-43.8	4300.5	4158.4
10.0	-46.2	-46.0	3401.3	3547.3
20.0	-49.2	-47.6	2337.0	2572.5
30.0	-51.4	-50.1	1725.3	2072.0
50.0	-53.0	-50.7	1416.9	1737.4
70.0	-55.6	-50.5	1055.1	1283.3
90.0	-56.7	-50.3	933.6	1127.1
100.0	-57.5	-50.4	849.7	1029.2
200.0	-60.8	-48.3	606.6	681.8
400.0	-63.8	-44.7	458.9	454.6
600.0	-65.1	-42.1	412.5	373.0
800.0	-65.6	-40.2	400.9	339.0
1000.0	-65.8	-32.7	431.7	277.3
2000.0	-66.3	-26.7	432.7	217.7
3000.0	-70.3	-28.2	269.3	144.4
5000.0	-71.0	-25.3	254.8	120.5
7000.0	-71.7	-23.7	238.1	104.6
9000.0	-71.8	-22.2	238.0	97.2
10000.0	-71.7	-21.6	241.8	95.8
20000.0	-72.0	-18.2	238.7	78.5
40000.0	-71.8	-14.8	248.6	65.7
60000.0	-72.1	-13.1	241.9	56.3
80000.0	-71.9	-12.0	248.6	52.8
100000.0	-72.3	-11.0	238.3	46.3

Table 5.10 Components of the impedance at 823 K when the pressure on the inside of the sensor was 114 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
1.0	-36.0	-32.1	13534.6	8651.8
2.0	-38.2	-37.5	9798.6	7637.4
3.0	-39.7	-41.0	7826.5	6898.3
5.0	-41.8	-44.5	5798.3	5763.8
7.0	-43.4	-46.3	4668.5	4933.7
10.0	-45.1	-47.7	3738.4	4142.5
20.0	-48.4	-49.4	2471.8	2901.0
30.0	-50.7	-51.2	1826.2	2282.0
50.0	-53.2	-51.9	1348.8	1726.3
60.0	-53.9	-48.6	1334.3	1518.1
80.0	-55.4	-51.3	1061.2	1328.2
100.0	-56.3	-50.6	971.3	1185.4
200.0	-60.3	-49.0	633.7	730.0
300.0	-62.2	-46.8	531.4	566.4
500.0	-64.0	-43.4	458.5	433.9
700.0	-64.9	-41.2	428.1	375.0
1000.0	-65.2	-33.3	459.4	302.0
2000.0	-69.1	-31.4	299.4	182.8
4000.0	-70.3	-26.6	273.2	136.9
6000.0	-71.0	-24.4	271.7	116.5
8000.0	-71.2	-22.8	255.9	106.8
10000.0	-71.4	-21.8	250.0	100.0
20000.0	-74.7	-19.1	174.0	60.3
30000.0	-75.1	-17.0	168.1	51.4
50000.0	-75.9	-14.6	155.2	40.4
70000.0	-75.8	-12.9	158.1	36.2
100000.0	-76.0	-11.2	155.5	30.8

Table 5.11 Components of the impedance at 673 K when the pressure on the inside of the sensor was 760 torr

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z''(ohms)
1.0	-19.1	-47.1	73379.8	94337.0
2.0	-22.3	-51.6	45880.2	66044.6
3.0	-24.4	-50.0	37897.4	49838.8
4.0	-26.0	-50.0	31663.0	40927.7
5.0	-26.8	-49.9	28998.9	37067.5
6.0	-27.8	-49.9	25896.0	32828.5
7.0	-28.6	-49.4	23921.2	29600.3
8.0	-29.2	-49.1	22493.7	27420.4
9.0	-29.7	-48.7	21435.3	25674.3
10.0	-30.3	-48.2	20233.0	23717.6
15.0	-32.1	-46.7	16980.4	18697.1
20.0	-33.1	-44.7	15728.4	16063.8
30.0	-35.0	-43.4	12934.2	12538.1
40.0	-36.2	-41.9	11551.9	10585.2
50.0	-37.1	-40.7	10613.8	9300.8
60.0	-37.3	-39.0	10642.5	8772.2
70.0	-38.3	-39.0	9481.6	7800.2
80.0	-38.8	-38.4	9027.4	7261.5
100.0	-39.6	-37.2	8369.5	6437.8
200.0	-42.0	-33.9	6616.8	4489.2
300.0	-43.3	-31.0	5884.3	3563.9
400.0	-44.4	-29.2	5278.9	2970.8
600.0	-45.5	-26.7	4759.6	2408.3
800.0	-46.2	-24.9	4458.0	2080.5
1000.0	-46.7	-23.0	4271.3	1822.2
2000.0	-48.0	-18.9	3779.1	1299.3
4000.0	-48.9	-15.8	3464.6	984.0
6000.0	-49.4	-14.6	3289.1	859.8
8000.0	-49.7	-14.0	3185.6	797.0
10000.0	-50.0	-13.7	3081.2	753.5

Cont'd..

20000.0	-50.5	-13.7	2908.4	711.1
30000.0	-50.8	-14.8	2795.5	740.8
40000.0	-51.0	-16.0	2715.9	781.1
50000.0	-51.2	-17.3	2635.9	823.3
70000.0	-51.6	-20.0	2477.0	904.1
90000.0	-51.9	-22.6	2350.4	981.0
100000.0	-52.1	-23.8	2276.2	1006.7
200000.0	-54.1	-33.5	1645.2	1092.2
300000.0	-55.8	-37.4	1289.1	987.6
500000.0	-58.4	-37.7	951.6	736.6
600000.0	-59.1	-36.8	888.5	665.6
700000.0	-59.8	-34.8	840.7	585.0
800000.0	-60.2	-33.0	820.0	533.1
900000.0	-60.6	-31.9	792.7	494.0
1000000	-60.8	-29.3	795.8	447.0
1500000	-61.6	-16.7	797.3	239.4
2000000	-62.0	-15.6	765.6	213.9

Table 5.12 Components of the impedance at 673 K when the pressure on the inside of the sensor was 370 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
1.0	-17.5	-46.0	89906.8	115226.5
2.0	-20.9	-51.4	53728.5	78667.8
3.0	-23.0	-51.0	43172.1	60070.4
4.0	-24.7	-51.0	35742.9	48637.5
6.0	-26.8	-51.1	28174.0	37656.5
8.0	-27.7	-50.7	25700.4	33587.0
10.0	-28.9	-50.6	22488.3	29018.8
20.0	-32.3	-51.8	14854.6	19647.1
40.0	-35.7	-45.0	11597.3	11872.7
60.0	-38.4	-42.0	8948.9	8189.9
80.0	-38.5	-40.8	9016.9	7907.3
100.0	-39.4	-39.5	8289.2	6929.8
200.0	-42.0	-35.6	6479.0	4684.4
400.0	-44.3	-31.7	5202.7	3236.3
600.0	-45.6	-29.3	4591.0	2592.0
800.0	-46.4	-27.5	4258.7	2228.9
1000.0	-46.9	-24.5	4125.2	1889.2
2000.0	-48.4	-20.2	3579.0	1322.1
4000.0	-49.5	-16.6	3219.4	963.2
6000.0	-50.0	-15.2	3060.3	834.3
8000.0	-50.3	-14.6	2964.5	774.6
10000.0	-50.5	-14.2	2902.0	736.6
20000.0	-51.2	-14.2	2676.7	679.2
30000.0	-51.4	-15.2	2603.7	709.4
40000.0	-51.6	-16.4	2529.0	746.4
60000.0	-52.0	-19.2	2377.2	830.0
80000.0	-52.3	-22.0	2254.2	913.2
100000.0	-52.8	-22.9	2114.0	895.1
200000.0	-54.7	-32.5	1553.9	992.1

Contd..

400000.0	-57.9	-37.5	1010.7	776.8
500000.0	-58.6	-36.3	947.3	696.9
600000.0	-59.4	-35.2	876.0	618.7
700000.0	-59.9	-34.1	838.0	568.1
800000.0	-60.5	-32.3	798.4	505.3
1000000	-60.8	-29.2	796.6	445.6
1500000	-61.7	-16.7	788.1	236.6
2000000	-61.8	-12.9	792.9	181.8

Table 5.13 Components of the impedance at 673 K when the pressure on the inside of the sensor was 137 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z''(ohms)
1.0	-18.8	-42.7	84315.8	92209.1
2.0	-21.9	-45.9	55289.2	64501.7
4.0	-25.6	-47.4	35170.8	41461.7
6.0	-26.7	-48.8	30087.1	36964.0
8.0	-28.4	-51.9	23063.5	31343.4
10.0	-29.6	-52.4	19890.0	27309.0
20.0	-32.8	-57.0	12250.9	19694.2
30.0	-34.6	-46.8	12720.5	13923.7
50.0	-36.9	-43.1	10444.9	9969.5
70.0	-38.3	-41.1	9183.5	8142.6
90.0	-39.4	-39.5	8289.2	6929.8
100.0	-39.7	-39.0	8066.5	6620.3
200.0	-42.2	-35.0	6379.1	4509.2
400.0	-44.4	-30.9	5187.7	3126.7
700.0	-45.9	-27.6	4507.8	2370.2
1000.0	-46.9	-23.7	4151.3	1831.5
2000.0	-48.3	-19.5	3636.8	1293.1
4000.0	-49.3	-16.2	3301.4	962.6
6000.0	-49.8	-15.0	3134.8	842.7
8000.0	-50.1	-14.3	3037.8	776.9
10000.0	-50.4	-13.9	2939.6	729.8
20000.0	-50.8	-14.1	2804.4	706.5
30000.0	-51.2	-15.2	2664.5	726.0
40000.0	-51.4	-16.5	2586.7	768.3
60000.0	-51.8	-19.3	2431.1	853.7
80000.0	-52.2	-22.0	2280.3	923.8
100000.0	-52.5	-24.5	2161.6	987.6
200000.0	-54.5	-33.9	1564.8	1053.9
400000.0	-57.7	-36.7	1045.3	780.4
500000.0	-58.7	-36.8	930.4	697.0

Contd..

600000.0	-59.4	-25.0	971.9	453.7
700000.0	-59.9	-21.8	940.0	376.3
900000.0	-60.8	-19.5	860.3	305.0
1000000	-60.7	-14.8	892.7	236.1
2000000	-62.1	-10.1	773.6	137.9

Table 5.14 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 723 K when the pressure on the inside of the sensor was 760 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z"(ohms)
0.01	*	-11.5	406160	119540
0.02		-14.5	359420	130590
0.04		-18.7	296140	135850
0.06		-22.3	261330	143900
0.08		-26.2	222010	143860
0.1		-27.4	206480	139090
0.2		-36.2	135000	123040
0.4		-41.8	89910.0	95671.0
0.6		-44.4	70833.0	80711.0
0.8		-44.9	59757.0	67647.0
1.0		-51.8	41823.0	59889.0
1.5		-48.6	39045.0	48689.0
2.0		-62.6	19436.0	41598.0
1.0	-23.4	-49.1	43332.0	55786.1
1.5	-25.2	-50.6	34138.0	45499.9
2.0	-26.6	-51.7	28383.6	38876.2
2.5	-27.6	-51.9	25240.5	34520.5
3.0	-28.5	-51.8	22859.9	30928.3
4.0	-30.0	-53.4	18535.6	26354.1
5.0	-30.8	-53.4	16932.6	23956.9
6.0	-31.8	-53.5	15080.5	21298.9
7.0	-32.5	-53.4	13964.1	19580.0
8.0	-33.3	-53.4	12750.4	17813.3
9.0	-33.5	-53.3	12493.4	17376.2
10.0	-34.5	-53.2	11304.6	15608.0
15.0	-36.6	-52.2	9008.3	11900.5
20.0	-38.0	-52.0	7710.5	10075.2
30.0	-40.1	-50.4	6282.4	7713.3

Contd..

40.0	-41.6	-49.2	5424.5	6365.4
60.0	-43.8	-48.4	4281.6	4869.8
80.0	-44.9	-45.6	3979.1	4096.8
100.0	-45.9	-44.2	3635.3	3560.2
200.0	-48.7	-40.3	2803.4	2388.9
300.0	-50.3	-38.0	2409.6	1889.9
400.0	-51.6	-36.4	2119.1	1567.5
600.0	-53.0	-34.1	1855.7	1259.8
800.0	-54.1	-32.6	1663.3	1066.2
1000.0	-54.7	-31.4	1572.8	962.1
2000.0	-56.7	-26.2	1313.3	647.3
3000.0	-57.6	-23.6	1209.2	529.0
5000.0	-58.5	-20.7	1112.8	421.0
7000.0	-59.1	-18.7	1051.6	356.4
8000.0	-59.3	-17.9	1032.4	333.9
10000	-59.6	-16.9	1002.8	305.0
20000	-60.5	-14.1	916.4	230.4
30000	-60.9	-13.1	878.9	204.7
40000	-61.1	-12.6	860.5	192.5
50000	-61.3	-9.5	849.9	142.3
60000	-61.6	-9.0	822.2	130.3
80000	-61.8	-8.6	804.3	121.7
100000	-61.9	-8.6	795.1	120.3
200000	-62.4	-8.2	751.4	108.4
300000	-62.6	-7.9	734.8	102.0
500000	-62.6	-7.5	735.5	96.9
600000	-62.9	-8.0	709.7	99.8
700000	-62.8	-8.4	717.2	106.0
800000	-62.6	-8.5	733.7	109.7
1000000	-62.7	-8.0	726.2	102.1

* These measurements were made with Lissajous figures.

Table 5.15 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 723 K when the pressure on the inside of the sensor was 510 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
0.01	*	-11.5	406161	119502
0.04		-19.1	309115	147575
0.08		-25.0	238646	147749
0.1		-26.9	213942	141793
0.3		-38.4	116694	113433
0.7		-47.5	62704	79562
1.0		-53.1	43011	65546
1.5	-24.6	-53.5	33811.3	50709.8
2.0	-26.2	-54.4	27622.7	42125.6
3.0	-28.4	-52.5	22717.9	31577.8
5.0	-31.2	-52.8	16428.6	22675.7
7.0	-33.0	-54.9	12692.1	18791.1
8.0	-33.7	-54.4	11877.7	17200.1
9.0	-34.3	-54.6	11036.7	16064.5
10.0	-34.5	-54.6	10788.5	15690.9
20.0	-38.2	-55.9	6839.7	10328.3
30.0	-40.5	-51.3	5882.5	7455.3
50.0	-43.0	-48.8	4656.3	5376.8
70.0	-44.5	-46.8	4075.3	4377.6
100.0	-46.0	-44.3	3587.5	3525.6
200.0	-48.9	-40.2	2743.5	2329.4
400.0	-51.3	-36.1	2202.2	1611.2
700.0	-53.1	-33.2	1853.9	1216.3
1000.0	-54.1	-31.4	1685.4	1031.1
2000.0	-56.4	-27.1	1348.7	691.4
4000.0	-57.3	-22.9	1258.4	532.3
7000.0	-59.0	-18.7	1063.8	360.5
10000.0	-59.5	-17.0	1013.9	310.3

Contd..

20000.0	-60.3	-14.4	936.5	240.7
40000.0	-60.9	-12.9	879.5	201.6
60000.0	-61.3	-12.5	841.3	186.7
80000.0	-61.4	-12.6	831.3	186.0
100000.0	-61.5	-12.5	822.1	182.4
200000.0	-62.2	-8.3	768.7	112.2
400000.0	-62.6	-8.3	734.1	107.2
600000.0	-62.9	-8.1	709.5	101.1
800000.0	-62.8	-8.3	717.3	104.7
1000000.0	-62.7	-7.7	726.7	98.3

* These measurements were done with Lissajous figures.

Table 5.16 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 723 K when the pressure on the inside of the sensor was 290 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z''(ohms)
0.01	*	-9.6	413004	100318
0.03		-16.1	336509	135297
0.05		-20.3	282707	141487
0.07		-20.3	261991	128344
0.1		-27.7	216523	150266
0.2		-32.9	157963	128938
0.4		-38.0	105387	98527
0.6		-43.0	80328	88107
0.8		-43.2	69229	74669
1.0		-40.3	65612	62666
1.0	-22.1	-49.1	50087	65703
2.0	-25.8	-53.3	29764	43682
3.0	-27.6	-53.5	24219	35194
4.0	-29.1	-52.8	20835	29138
6.0	-31.2	-54.4	15769	23119
7.0	-32.0	-54.0	14553.7	20926
8.0	-32.7	-54.4	13305.6	19355
9.0	-33.3	-54.2	12493.6	17987
10.0	-33.8	-54.3	11773.5	16977.9
20.0	-37.2	-54.2	8012.0	11377.0
30.0	-39.4	-53.9	6276.8	8767.4
50.0	-41.6	-53.7	4903.2	6769.5
70.0	-43.5	-52.1	4094.1	5317.1
90.0	-44.8	-50.5	3653.9	4472.7
100.0	-45.3	-50.1	3479.5	4196.7
300.0	-50.1	-41.4	2346.1	2077.0
500.0	-52.1	-36.9	1987.4	1496.8
700.0	-53.2	-34.2	1811.2	1234.1

Contd..



900.0	-54.0	-32.2	1690.1	1066.9
1000.0	-54.4	-31.4	1628.1	996.0
2000.0	-56.2	-26.5	1387.6	693.0
4000.0	-57.8	-21.9	1196.5	481.6
6000.0	-58.6	-19.5	1108.6	393.1
8000.0	-59.1	-18.0	1055.9	343.5
10000.0	-59.4	-16.9	1026.2	312.1
30000.0	-60.8	-10.1	898.7	160.2
50000.0	-61.3	-9.4	850.1	140.9
70000.0	-61.5	-9.0	831.7	131.8
90000.0	-61.7	-8.8	813.2	126.0
100000.0	-61.8	-8.8	803.9	124.6
300000.0	-62.4	-8.3	751.2	109.7
600000.0	-62.8	-8.3	717.3	104.7
800000.0	-62.8	-8.0	717.9	101.0
1000000.0	-62.6	-8.1	734.5	104.6

Table 5.17 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 773 K when the pressure on the inside of the sensor was 760 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	Z'' (ohms)
0.01		-7.4	149001.5	22979.4
0.02		-9.7	141043.9	28495.6
0.04		-15.0	126330.1	39424.3
0.06		-17.1	118070.8	41929.4
0.08		-16.6	114065.5	38990.9
0.1		-19.0	105565.5	41461.5
0.2		-26.7	86130.8	48877.2
0.3		-30.0	75086.8	48379.0
0.5		-34.5	59495.9	45056.5
0.7		-39.3	46529.0	41423.0
0.8		-40.9	43843.1	41306.0
0.9		-40.0	43053.5	39116.0
1.0		-38.0	41407.0	34715.5
1.5		-45.6	29551.7	32173.9
2.0		-40.5	30851.8	27920.0
3.0		-43.4	23641.4	23458.4
1.0	-26.6	-43.3	32901.2	33132.2
1.5	-28.3	-46.5	25635.2	28613.6
2.0	-29.6	-47.0	21958.7	24748.1
3.0	-31.6	-53.0	15370.0	21329.4
4.0	-32.9	-53.3	13192.3	18396.5
5.0	-34.0	-53.2	11688.5	16163.2
6.0	-34.9	-53.6	10460.0	14630.0
7.0	-35.8	-54.3	9286.6	13292.6
8.0	-36.5	-54.6	8515.5	12300.0
9.0	-37.1	-54.8	7916.1	11500.6
10.0	-37.7	-55.1	7339.6	10766.1
12.0	-38.6	-54.4	6746.9	9617.7

Contd..

15.0	-39.9	-55.7	5629.8	8403.8
20.0	-41.8	-55.7	4535.0	6745.3
30.0	-43.9	-55.2	3615.1	5260.2
40.0	-45.4	-54.9	3068.5	4407.3
50.0	-46.7	-54.7	2657.7	3783.8
60.0	-47.5	-53.1	2520.4	3380.7
70.0	-48.2	-54.4	2254.8	3170.6
80.0	-48.9	-54.1	2096.1	2913.6
90.0	-49.5	-53.7	1975.8	2704.8
100.0	-50.1	-53.4	1857.6	2514.3
200.0	-53.8	-50.5	1296.3	1577.5
300.0	-55.8	-48.1	1081.7	1208.5
500.0	-58.0	-44.6	895.6	884.7
700.0	-59.4	-42.0	795.8	717.6
1000.0	-60.7	-38.4	722.7	573.5
2000.0	-63.0	-32.8	594.9	383.7
3000.0	-64.2	-29.6	536.0	304.7
5000.0	-65.4	-26.1	482.2	236.4
7000.0	-66.5	-23.1	435.2	185.7
10000.0	-67.0	-21.7	415.0	165.2
20000.0	-68.3	-17.8	366.2	117.6
40000.0	-69.2	-14.2	336.1	85.1
60000.0	-69.6	-12.3	323.5	70.6
80000.0	-70.0	-7.5	313.5	41.3
100000	-70.1	-6.4	310.7	34.9
200000	-70.3	-2.0	305.3	10.7

Table 5.18 Real and Imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 773 K when the pressure on the inside of the sensor was 441 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
0.02		-10.7	152015.0	33207.0
0.05		-17.0	127900.9	44600.2
0.08		-19.5	108199.7	43046.0
0.1		-22.3	99998.2	46061.1
0.2		-28.4	79411.6	47649.4
0.4		-28.4	79418.7	47637.8
0.6		-40.0	45158.0	41028.0
0.8		-41.8	37463.5	35921.8
1.0		-44.1	34412.9	35710.1
1.0	-27.0	-45.1	31455.7	33696.9
2.0	-30.1	-50.4	19716.5	25061.0
3.0	-31.7	-51.8	15904.2	21097.0
4.0	-33.5	-51.6	13017.3	17002.0
5.0	-34.6	-51.4	11534.9	14893.0
6.0	-35.6	-52.6	10003.2	13451.8
7.0	-36.4	-54.6	8689.1	12554.7
8.0	-37.0	-55.3	7968.3	11800.5
9.0	-37.7	-55.1	7395.2	10847.6
10.0	-38.2	-54.6	7075.2	10171.7
15.0	-40.6	-56.1	5171.4	7827.0
20.0	-42.0	-53.3	4728.4	6429.2
30.0	-44.2	-55.7	3460.6	5129.2
40.0	-45.8	-55.2	2917.8	4236.1
50.0	-47.0	-54.8	2568.0	3668.8
60.0	-48.4	-53.2	2273.2	3058.1
70.0	-48.9	-53.9	2110.7	2912.3
80.0	-49.5	-53.5	1989.2	2703.3
90.0	-50.2	-53.0	1857.1	2477.2

Contd..

100.0	-50.7	-52.6	1769.7	2325.9
200.0	-54.2	-49.4	1268.3	1484.2
300.0	-56.1	-46.9	1070.4	1146.4
500.0	-58.4	-43.5	872.2	829.0
800.0	-60.2	-40.0	748.8	629.1
1000.0	-61.0	-38.3	699.6	553.1
2000.0	-63.1	-31.0	600.1	360.9
4000.0	-65.1	-27.0	495.5	252.6
6000.0	-66.0	-24.4	456.6	207.2
8000.0	-66.6	-22.6	432.0	179.9
10000.0	-67.0	-21.2	416.6	161.7
20000.0	-68.4	-17.3	363.1	113.1
50000.0	-69.4	-12.9	330.4	75.7
80000.0	-69.9	-10.5	314.6	58.3
100000.0	-70.1	-6.2	310.9	33.8
200000.0	-70.5	-2.0	298.4	10.4

Table 5.19 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 773 K when the pressure on the inside of the sensor was 248 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z"(ohms)
0.01		-7.2	188019	28244
0.03		-12.4	157018	40199
0.05		-16.3	134573	45120
0.08		-20.4	118596	50142
0.1		-21.3	111965	49550
0.2		-30.0	81962.7	52810
0.4		-34.9	59040.6	44941
0.6		-38.7	47517.7	41211
0.8		-36.9	40649.7	32519
1.0		-41.8	33709.3	32089
1.0	-27.6	-46.9	28310.0	32218
2.0	-31.3	-51.2	16882.3	21952
3.0	-33.1	-52.3	13399.7	17988
4.0	-34.5	-51.1	11748.1	15009
5.0	-35.7	-53.3	9723.0	13413
6.0	-36.7	-53.3	8673.8	11929
8.0	-38.2	-53.9	7200.3	10085
10.0	-39.4	-53.4	6354.6	8712.4
15.0	-41.7	-53.9	4823.2	6708.1
20.0	-43.4	-53.4	4017.7	5471.4
30.0	-45.3	-54.4	3152.9	4445.2
50.0	-47.7	-53.6	2440.5	3333.1
70.0	-49.7	-52.5	1989.9	2607.3
90.0	-51.0	-51.6	1748.8	2216.5
100.0	-51.5	-51.0	1673.0	2074.7
200.0	-55.0	-47.6	1198.8	1316.3
400.0	-58.0	-43.1	919.3	861.8
700.0	-60.2	-37.2	778.6	591.8

Contd..

1000.0	-61.4	-34.6	700.8	484.0
2000.0	-63.4	-29.4	589.3	332.3
5000.0	-65.9	-24.5	461.5	210.4
8000.0	-67.0	-21.6	415.4	164.6
10000.0	-67.3	-20.3	404.8	149.8
20000.0	-68.7	-16.6	352.1	105.
40000.0	-69.3	-13.4	333.5	79.5
60000.0	-69.7	-11.7	320.6	66.4
80000.0	-69.9	-10.4	314.7	57.8
100000.0	-70.2	-5.9	307.5	31.8
200000.0	-70.5	-1.7	298.5	8.9

Table 5.20 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 773 K when the pressure on the inside of the sensor was 132 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z"(ohms)
0.01		-7.7	173966.6	27571.0
0.02		-11.1	161349.8	37127.7
0.04		-13.9	149172.9	43033.3
0.06		-18.3	135365.7	51709.6
0.08		-18.7	132012.1	51354.9
0.1		-22.5	118902.3	56481.0
0.2		-28.4	93525.9	56958.9
0.4		-36.9	61397.7	50810.8
0.6		-38.0	52129.9	44355.8
0.8		-39.5	42914.7	38118.3
1.0		-40.5	38313.3	35076.1
1.0	-27.6	-47.4	28011.4	32460.6
2.0	-30.8	-52.4	17362.3	23663.2
3.0	-32.8	-54.4	13155.5	19127.4
4.0	-34.2	-53.2	11565.1	15980.0
5.0	-35.4	-54.8	9687.4	14150.0
6.0	-36.3	-53.5	9035.7	12532.7
7.0	-37.1	-54.6	8022.2	11567.0
8.0	-37.8	-54.9	7349.3	10696.9
9.0	-38.5	-55.0	6766.7	9868.8
10.0	-39.1	-55.5	6237.0	9255.8
15.0	-41.3	-55.5	4849.5	7164.8
20.0	-42.4	-57.9	4005.4	6477.8
30.0	-45.0	-55.0	3214.3	4636.2
40.0	-46.6	-54.4	2715.8	3823.9
50.0	-47.7	-53.7	2434.6	3337.4
60.0	-47.3	-50.6	2735.2	3352.7
70.0	-49.5	-53.2	2003.2	2692.9

Contd..

80.0	-51.1	-52.8	1682.4	2226.7
100.0	-51.2	-52.0	1693.8	2177.8
200.0	-54.8	-48.2	1212.5	1359.9
400.0	-57.9	-43.5	923.9	878.2
700.0	-60.0	-39.5	771.8	637.1
1000.0	-61.3	-34.8	707.3	492.1
2000.0	-63.5	-30.8	574.3	342.6
4000.0	-65.3	-26.0	488.5	238.4
7000.0	-66.5	-22.6	437.0	182.0
10000.0	-67.1	-20.5	413.7	154.8
20000.0	-68.2	-16.8	372.6	112.5
50000.0	-69.1	-12.9	342.0	78.4
70000.0	-69.5	-11.6	328.2	67.4
100000.0	-69.7	-3.7	326.8	21.1
200000.0	-69.8	-0.3	323.7	1.7

Table 5.21 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 823 K when the pressure on the inside of the sensor was 760 torr. $R_s = 1 \text{ M}\Omega$

Freq (Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z*(ohms)
0.05		-6.2	39816.5	4503.8
0.08		-9.3	39484.4	6755.4
0.1		-12.5	39015.9	8994.3
0.3		-20.2	29065.0	11031.1
0.5		-25.0	25015.2	12041.0
0.6		-28.6	22294.3	12497.7
0.7		-28.6	21351.9	11954.8
0.8		-27.0	20723.1	10853.8
0.9		-27.0	20723.1	10853.8
1.0		-30.0	18259.2	10801.8
1.0	-35.1	-35.6	14391.8	10531.6
1.5	-36.4	-38.5	11895.0	9648.2
2.0	-37.5	-41.0	10087.5	8926.9
3.0	-39.2	-43.8	7917.9	7710.3
4.0	-40.3	-45.4	6781.1	6972.6
5.0	-41.2	-47.4	5888.5	6487.0
6.0	-42.3	-48.5	5077.0	5805.9
7.0	-42.9	-47.6	4824.1	5339.8
8.0	-43.5	-48.0	4467.2	5011.5
9.0	-44.1	-48.6	4119.8	4717.5
10.0	-44.6	-48.9	3865.9	4471.6
20.0	-48.0	-52.1	2441.5	3156.7
30.0	-49.9	-52.0	1966.9	2530.8
40.0	-51.5	-52.3	1625.3	2112.0
50.0	-52.6	-52.6	1422.3	1867.6
60.0	-54.2	-55.0	1117.0	1600.8
70.0	-54.4	-52.6	1156.3	1517.3
80.0	-55.0	-52.5	1081.7	1413.8

Contd..

90.0	-55.7	-52.4	1000.3	1302.4
100.0	-56.0	-52.3	968.5	1256.4
200.0	-59.6	-50.6	664.4	810.2
300.0	-61.7	-48.7	542.6	618.4
400.0	-63.1	-47.2	475.5	514.0
600.0	-65.0	-44.8	399.0	396.6
800.0	-66.2	-42.9	358.8	333.6
1000.0	-67.0	-41.4	335.1	295.6
2000.0	-69.4	-34.1	280.6	190.1
3000.0	-70.8	-32.1	244.3	153.3
5000.0	-72.2	-28.6	215.6	117.6
7000.0	-73.1	-26.3	198.4	98.1
10000.0	-73.9	-23.9	184.6	81.8
20000.0	-75.2	-19.4	163.9	57.7
30000.0	-75.7	-16.9	157.0	47.7
50000.0	-76.2	-14.0	150.3	37.5
70000.0	-76.5	-12.3	146.2	31.9
90000.0	-76.4	-10.8	148.7	28.4
100000.0	-76.9	-3.5	142.6	8.7

Table 5.22 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 823 K when the pressure on the inside of the sensor was 529 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z''(ohms)
0.01		-2.5	50273.9	2296.9
0.02		-5.0	50107.0	4595.7
0.05		-11.0	44791.2	9096.8
0.08		-11.5	42483.8	9057.7
0.1		-15.3	39586.1	11261.5
0.2		-20.7	34101.6	13365.8
0.4		-26.6	27554.7	14300.1
0.6		-27.5	24450.4	13117.7
0.8		-31.5	20698.9	13024.7
1.0		-33.1	19416.5	12994.2
1.0	-34.5	-35.9	15367.4	11388.6
1.5	-36.0	-39.6	12256.8	10353.2
2.0	-37.2	-42.8	10140.9	9571.0
3.0	-38.8	-43.8	8291.2	8079.7
5.0	-41.2	-46.9	5945.7	6435.6
7.0	-42.8	-48.3	4812.8	5461.3
9.0	-43.9	-49.1	4172.8	4864.8
10.0	-44.5	-50.2	3806.5	4611.5
15.0	-46.4	-51.2	2994.0	3752.7
20.0	-48.5	-53.4	2236.8	3030.7
30.0	-50.0	-51.8	1953.2	2494.7
40.0	-51.4	-52.5	1636.6	2142.3
50.0	-52.6	-53.0	1409.2	1877.5
60.0	-54.1	-51.3	1232.4	1543.2
70.0	-54.3	-53.0	1159.0	1543.0
80.0	-55.0	-52.8	1074.3	1419.5
90.0	-55.7	-52.6	995.7	1305.9
100.0	-56.2	-52.5	942.2	1231.0
150.0	-58.3	-51.5	756.7	953.2

200.0	-59.8	-50.5	650.7	790.6
300.0	-61.7	-48.6	543.7	617.5
400.0	-63.0	-47.0	482.8	518.2
500.0	-63.8	-45.7	450.9	462.5
700.0	-65.5	-43.7	383.8	367.0
900.0	-66.5	-42.0	351.7	316.8
1000.0	-67.0	-41.3	335.6	295.0
2000.0	-69.3	-36.4	275.9	203.5
4000.0	-70.8	-31.8	245.2	152.1
7000.0	-72.0	-26.3	225.2	111.3
10000.0	-73.7	-23.9	188.9	83.7
20000.0	-74.9	-19.6	169.5	60.4
40000.0	-75.8	-15.5	156.3	43.4
60000.0	-76.2	-13.1	150.9	35.1
80000.0	-76.4	-11.6	148.3	30.4
100000	-76.5	-3.3	149.4	8.6

Table 5.23 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 823 K when the pressure on the inside of the sensor was 332 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
0.01		-5.1	48956.4	4583.7
0.03		-7.7	48676.6	6872.0
0.05		-9.4	46174.4	7980.4
0.08		-11.5	42483.8	9060.4
0.1		-14.9	40749.3	11287.0
0.2		-20.1	35289.2	13398.9
0.4		-23.6	29314.7	13246.6
0.6		-27.5	24450.4	13117.7
0.8		-30.0	21963.0	13057.2
1.0		-33.1	19419.5	12989.9
1.0	-34.2	-36.6	15760.5	11997.0
2.0	-36.8	-42.9	10601.9	10050.2
3.0	-38.6	-44.3	8411.0	8345.0
4.0	-40.0	-44.9	7082.8	7159.4
5.0	-40.8	-47.4	6165.7	6796.5
6.0	-41.6	-48.6	5491.4	6308.2
7.0	-42.3	-48.6	5066.9	5814.8
8.0	-43.0	-49.2	4618.4	5409.1
9.0	-43.5	-49.6	4324.4	5133.9
10.0	-44.1	-49.7	4027.7	4795.7
15.0	-46.1	-51.3	3092.3	3890.8
20.0	-47.0	-54.1	2612.9	3637.4
30.0	-49.6	-53.5	1966.5	2672.2
40.0	-51.2	-53.1	1651.5	2209.8
50.0	-52.3	-53.0	1458.7	1943.7
60.0	-52.8	-57.3	1235.4	1932.5

Contd..

70.0	-54.2	-53.2	1166.9	1564.9
80.0	-54.9	-53.1	1079.1	1441.6
90.0	-55.5	-53.0	1009.5	1343.5
100.0	-56.0	-52.9	955.3	1266.5
200.0	-59.6	-50.8	661.6	812.6
300.0	-61.5	-49.1	550.8	636.7
500.0	-63.7	-45.9	454.5	469.5
700.0	-64.9	-43.7	411.3	393.3
1000.0	-66.7	-39.6	356.3	295.0
2000.0	-69.1	-34.1	290.5	196.8
4000.0	-70.7	-28.9	255.5	141.1
7000.0	-72.0	-25.6	226.6	108.6
10000.0	-73.6	-24.0	190.9	85.0
20000.0	-74.9	-19.6	169.5	60.4
40000.0	-75.8	-15.4	156.4	43.1
70000.0	-76.2	-12.3	151.3	33.0
90000.0	-76.6	-3.8	147.6	9.8
100000.0	-76.6	-3.3	147.7	8.5

Table 5.24 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 823 K when the pressure on the inside of the sensor was 201 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
0.03		-6.5	47670.7	5735.4
0.06		-9.4	46165.7	7990.8
0.08		-12.4	44537.3	10214.2
0.1		-14.5	41917.6	11309.6
0.2		-19.5	36477.7	13416.0
0.4		-27.8	28187.4	15430.9
0.6		-28.8	25066.2	14248.6
0.8		-32.8	21265.1	14134.9
1.0		-33.0	19427.0	12979.9
1.0	-34.1	-37.3	15790.4	12335.5
2.0	-36.8	-43.8	10439.0	10215.5
4.0	-39.6	-45.7	7309.9	7604.7
6.0	-41.6	-46.1	5764.5	6063.1
8.0	-42.9	-49.2	4671.8	5472.3
10.0	-44.0	-51.2	3944.7	4956.4
20.0	-47.7	-52.4	2510.1	3281.5
30.0	-49.4	-53.2	2026.4	2724.2
40.0	-51.0	-53.4	1678.2	2270.2
60.0	-52.5	-53.0	1425.5	1899.3
70.0	-54.0	-53.5	1185.7	1607.7
80.0	-54.7	-53.3	1099.1	1479.1
90.0	-55.3	-53.3	1025.8	1380.2
100.0	-55.8	-53.2	970.7	1301.1
200.0	-59.4	-51.0	674.1	833.9
300.0	-61.4	-49.4	553.8	647.0
400.0	-62.8	-47.7	487.5	536.3
600.0	-64.6	-45.2	414.9	418.2
800.0	-65.8	-43.2	373.9	351.4

Contd..

1000.0	-66.7	-41.7	345.3	307.8
2000.0	-69.1	-34.3	289.8	197.8
4000.0	-70.6	-29.0	258.2	143.1
7000.0	-71.9	-25.6	229.2	109.8
10000.0	-72.3	-23.3	222.9	96.0
20000.0	-74.9	-19.7	169.4	60.7
30000.0	-75.4	-17.1	162.3	50.0
50000.0	-76.0	-14.1	153.7	38.6
70000.0	-76.3	-12.3	149.6	32.6
100000.0	-76.8	-3.4	144.3	8.6

Table 5.25 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 855 K when the pressure on the inside of the sensor was 760 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
0.08		4.8	12102.0	1020.4
0.1		7.8	11016.0	1529.0
0.2		13.1	10822.0	2551.2
0.4		14.5	9770.9	2549.7
0.6		19.5	8549.8	3048.6
0.8		19.5	8549.8	3048.6
0.9		22.9	8348.1	3559.5
1.0		24.3	7793.1	3556.7
1.0	-41.2	-24.4	7981.9	3655.5
1.5	-42.2	-28.6	6848.1	3767.0
2.0	-43.0	-30.8	6104.7	3669.3
3.0	-44.3	-32.6	5150.7	3317.9
4.0	-45.1	-34.4	4598.1	3169.5
5.0	-45.9	-36.9	4061.4	3068.8
7.0	-47.3	-38.9	3362.2	2728.2
9.0	-48.3	-40.4	2931.1	2507.3
10.0	-48.8	-41.4	2725.2	2414.2
15.0	-50.5	-44.0	2147.9	2082.7
20.0	-51.3	-43.6	1972.1	1885.1
30.0	-53.6	-46.4	1440.6	1517.4
40.0	-54.9	-47.8	1208.0	1335.8
50.0	-56.0	-48.2	1056.1	1184.0
60.0	-57.2	-54.3	804.9	1122.8
70.0	-57.7	-49.0	854.7	985.2
80.0	-58.3	-49.2	794.5	922.1
90.0	-59.0	-49.3	731.5	851.9
100.0	-59.5	-49.2	692.0	803.0
200.0	-62.9	-49.4	466.0	544.3
300.0	-64.8	-48.5	381.2	431.3
400.0	-66.2	-47.6	330.2	361.9
600.0	-68.0	-45.8	277.5	285.6

Contd..

800.0	-69.2	-44.2	248.6	241.8
1000.0	-70.0	-39.6	243.7	201.7
2000.0	-73.1	-36.5	177.9	131.7
4000.0	-75.1	-31.5	149.9	91.9
6000.0	-76.1	-28.8	137.3	75.5
8000.0	-76.8	-26.8	129.0	65.2
10000.0	-77.2	-25.4	124.7	59.2
20000.0	-77.9	-20.8	119.1	45.2
40000.0	-78.4	-16.3	115.4	33.7
60000.0	-78.6	-13.9	114.1	28.2
80000.0	-78.8	-12.1	112.3	24.1

Table 5.26 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 855 K when the pressure on the inside of the sensor was 436 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z'(ohms)	-Z''(ohms)
0.05		-2.5	11366	506.4
0.08		-3.8	11351	771.1
0.1		-5.2	11074	1023.3
0.2		-9.6	10457	1790.3
0.4		-13.0	9834.3	2294.2
0.6		-17.8	8634.6	2801.5
0.8		-20.1	8277.7	3051.2
0.9		-20.7	8007.0	3048.9
1.0		-22.0	7462.2	3045.0
1.0	-42.4	-21.9	7080.2	2869.6
1.5	-43.1	-25.9	6325.7	3095.9
2.0	-43.9	-29.4	5581.8	3168.4
3.0	-45.1	-33.2	4664.1	3072.3
4.0	-45.8	-34.3	4246.4	2914.8
5.0	-46.7	-37.3	3683.7	2822.8
6.0	-47.4	-39.1	3314.2	2708.2
8.0	-48.4	-38.9	2961.9	2401.7
10.0	-49.4	-39.6	2613.0	2171.3
20.0	-52.8	-45.5	1605.6	1639.2
30.0	-54.0	-45.6	1395.9	1429.6
50.0	-56.4	-47.5	1022.4	1118.2
70.0	-57.9	-48.6	842.0	956.9
90.0	-59.0	-48.9	737.4	846.7
100.0	-59.6	-49.5	679.9	797.3
200.0	-63.1	-49.4	455.4	531.9
300.0	-65.1	-48.7	366.8	417.9
400.0	-66.5	-47.8	317.8	350.7
500.0	-67.5	-46.8	288.7	307.6

Contd..

600.0	-68.3	-45.9	267.6	276.3
700.0	-68.9	-45.2	252.9	254.8
800.0	-69.5	-44.5	238.9	234.9
900.0	-69.9	-44.0	230.1	222.3
1000.0	-70.6	-41.8	220.0	196.8
2000.0	-73.2	-36.9	175.0	131.0
5000.0	-75.9	-30.1	138.7	80.4
7000.0	-76.6	-27.9	130.7	69.2
10000.0	-77.3	-25.4	123.3	58.5
20000.0	-78.3	-20.8	113.7	43.2
40000.0	-78.2	-16.4	118.0	34.7
60000.0	-78.8	-13.8	111.5	27.4
80000.0	-78.7	-12.1	113.6	24.3
100000.0	-78.9	-10.7	111.5	21.1

Table 5.27 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 855 K when the pressure on the inside of the sensor was 180 torr. $R_s = 1 \text{ M}\Omega$

Freq(Hz)	B/A(dB)	ϕ (deg)	Z' (ohms)	$-Z''$ (ohms)
0.2		-10.1	9940.3	1784.8
0.4		-14.5	8785.9	2289.7
0.6		-16.1	8715.3	2543.2
0.8		-20.7	8007.5	3047.9
1.0		-20.7	8007.5	3047.9
1.0	-42.0	-23.2	7344.6	3175.2
2.0	-43.8	-29.1	5663.6	3175.7
3.0	-44.9	-33.3	4767.4	3152.9
4.0	-46.0	-36.6	4030.7	3012.5
5.0	-46.5	-34.3	3916.9	2687.3
6.0	-47.2	-35.8	3546.3	2571.6
7.0	-47.8	-38.4	3196.4	2546.7
9.0	-48.8	-39.9	2787.7	2342.1
10.0	-49.3	-40.6	2604.3	2242.2
15.0	-51.0	-42.8	2068.5	1922.9
20.0	-51.9	-41.1	1915.6	1676.7
30.0	-54.0	-46.3	1378.3	1446.5
40.0	-55.4	-47.1	1155.8	1246.9
50.0	-56.4	-47.8	1016.4	1123.5
70.0	-58.0	-48.6	832.3	945.9
90.0	-59.3	-49.2	708.1	821.7
100.0	-59.7	-49.4	673.5	787.0
200.0	-61.9	-49.4	522.8	610.7
300.0	-65.1	-48.8	366.1	418.6
400.0	-66.5	-47.7	318.4	350.2
600.0	-68.3	-46.0	267.1	276.8
800.0	-69.4	-44.5	241.7	237.6

Contd..

1000.0	-70.2	-43.2	225.3	211.6
2000.0	-72.0	-34.2	207.8	141.2
4000.0	-75.5	-31.6	143.0	88.0
7000.0	-76.6	-27.9	130.7	69.2
10000.0	-77.1	-25.4	126.1	59.9
20000.0	-78.1	-20.8	116.4	44.2
40000.0	-78.2	-16.3	118.1	34.5
70000.0	-78.7	-12.9	113.2	25.9
100000.0	-78.6	-10.7	115.5	21.8

Table 5.28 Real and imaginary components of the impedance from the measurements on the gain phase meter and Lissajous figures at 823 K

Freq(Hz)	B/A(dB)	ϕ (deg)	R_s (ohms)	Z' (ohms)	$-Z''$ (ohms)
0.005	*	-3.24	4.00E6	49790.0	2850.6
0.008		-4.63	4.00E6	49705.0	4070.9
0.01		-5.22	4.00E6	48441.0	4471.8
0.02		-8.36	4.00E6	46507.0	6915.2
0.03		-10.8	4.00E6	44168.0	8521.8
0.04		-12.3	4.00E6	42340.0	9333.2
0.05		-13.8	4.00E6	40895.0	10154.0
0.06		-15.1	4.00E6	38703.0	10530.0
0.07		-16.3	4.00E6	38461.0	11364.0
0.08		-17.5	4.00E6	38212.0	12175.0
0.09		-18.6	4.00E6	35669.0	12124.0
0.1		-20.2	2.00E6	32894.0	12329.0
0.2		-27.8	2.00E6	26600.0	14277.0
0.3		-33.2	2.00E6	21414.0	14202.0
0.4		-35.9	2.00E6	18747.0	13762.0
0.5		-36.3	2.00E6	17347.0	12934.0
0.6		-39.2	2.00E6	15112.0	12500.0
0.7		-40.7	2.00E6	13875.0	12084.0
0.8		-42.4	2.00E6	12624.0	11667.0
0.9		-42.5	2.00E6	11726.0	10862.0
1.0	-43.0	-47.8	2.00E6	9454.7	10538.3
2.0	-46.4	-53.1	2.00E6	5717.9	7676.9
3.0	-48.6	-55.1	2.00E6	4232.8	6107.0
4.0	-50.2	-55.9	2.00E6	3452.1	5126.8
5.0	-51.4	-56.4	2.00E6	2968.9	4490.5
6.0	-52.4	-56.3	2.00E6	2654.1	3996.8
7.0	-53.2	-56.0	2.00E6	2440.2	3631.9
8.0	-53.9	-55.9	2.00E6	2257.7	3346.4
9.0	-54.6	-55.5	2.00E6	2104.7	3072.3
10.0	-55.1	-55.2	2.00E6	2002.5	2890.0
15.0	-57.3	-53.5	2.00E6	1621.0	2195.6
20.0	-58.7	-51.8	2.00E6	1434.8	1826.7
30.0	-60.7	-49.5	2.00E6	1197.4	1403.8

Contd..

40.0	-62.1	-47.7	2.00E6	1056.3	1162.2
60.0	-63.9	-44.6	2.00E6	908.5	896.7
80.0	-65.1	-43.1	2.00E6	811.5	760.0
100.0	-59.9	-41.8	1.00E6	753.7	674.7
200.0	-62.4	-38.0	1.00E6	597.6	467.3
300.0	-63.8	-36.2	1.00E6	520.9	381.5
400.0	-59.6	-34.7	5.00E5	430.3	298.3
600.0	-60.6	-33.3	5.00E5	389.9	256.4
800.0	-61.2	-32.4	5.00E5	367.6	233.5
1000.0	-61.7	-31.7	5.00E5	349.7	216.2
2000.0	-63.7	-29.6	5.00E5	283.9	161.4
4000.0	-57.9	-27.2	2.00E5	226.5	116.6
6000.0	-58.9	-25.6	2.00E5	204.7	98.2
8000.0	-59.3	-24.4	2.00E5	197.4	89.6
10000.0	-59.8	-23.4	2.00E5	187.8	81.4
20000.0	-61.2	-20.5	2.00E5	163.1	61.1
40000.0	-62.3	-18.2	2.00E5	145.8	48.0
60000.0	-62.8	-17.6	2.00E5	138.1	43.8
70000.0	-63.0	-17.5	2.00E5	135.0	42.6
80000.0	-63.1	-17.6	2.00E5	133.4	42.4
90000.0	-63.2	-17.7	2.00E5	131.8	42.1
100000.0	-63.4	-18.1	2.00E5	128.5	42.0
100000.0	-57.0	-18.7	1.00E5	133.8	45.3
200000.0	-57.6	-23.6	1.00E5	120.8	52.8
400000.0	-58.1	-37.0	1.00E5	99.3	75.0
600000.0	-58.6	-53.4	1.00E5	70.0	94.4
800000.0	-59.4	-70.5	1.00E5	35.7	101.0
1000000.0	-60.4	-87.8	1.00E5	3.6	95.4

* These measurements were done using Lissajous figures.

Table 5.29 Real and imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 773 K

Freq(Hz)	B/A(dB)	ϕ (deg)	R_1 (ohms)	Z' (ohms)	$-Z''$ (ohms)
0.002	*	-11.6	20.00E6	463003	95338
0.004		-15.9	20.00E6	405009	115206
0.006		-18.7	20.00E6	376353	127117
0.008		-20.6	20.00E6	349635	131103
0.009		-21.5	20.00E6	343859	135065
0.01		-21.5	20.00E6	332616	131090
0.02		-26.7	20.00E6	276906	139029
0.03		-31.5	20.00E6	225949	139035
0.04		-34.1	20.00E6	194287	131084
0.05		-36.1	20.00E6	179727	131089
0.05		-35.5	10.00E6	169748	121158
0.06		-37.8	10.00E6	153902	119172
0.07		-39.1	10.00E6	141844	115199
0.08		-40.9	10.00E6	130547	113213
0.09		-41.8	10.00E6	119910	107260
0.1		-41.8	10.00E6	115473	103283
0.2		-47.1	10.00E6	75763.1	81434.1
0.3		-50.6	10.00E6	55474.6	67528.6
0.4		-52.1	10.00E6	46323.3	59588.2
0.5		-49.9	10.00E6	43515.3	51641.6
0.6		-47.9	10.00E6	41284.6	45680.6
0.7		-51.1	10.00E6	33706.9	41710.3
0.8		-50.3	10.00E6	32991.8	39724.1
0.9		-44.1	10.00E6	32815.4	31781.5
1.0		-50.6	10.00E6	27737.4	33764.3
1.0	-35.9	-49.6	3.00E6	31173.5	36627.9
1.5	-37.8	-50.2	3.00E6	24739.7	29693.3
1.5	-34.8	-50.5	2.00E6	23150.5	28081.9
2.0	-36.4	-50.5	2.00E6	19255.8	23357.5
3.0	-38.4	-49.1	2.00E6	15743.0	18174.9

Contd..

4.0	-39.8	-49.2	2.00E6	13373.3	15493.0
4.0	-35.0	-50.5	1.00E6	11311.8	13721.3
5.0	-35.9	-49.2	1.00E6	10476.3	12136.9
6.0	-36.6	-48.6	1.00E6	9781.6	11095.1
7.0	-37.4	-47.8	1.00E6	9060.9	9992.9
8.0	-38.0	-47.1	1.00E6	8569.8	9222.2
9.0	-38.6	-46.4	1.00E6	8102.5	8508.4
10.0	-39.0	-45.7	1.00E6	7836.5	8030.3
20.0	-42.2	-40.5	1.00E6	5902.4	5041.5
20.0	-42.1	-41.5	1.00E6	5881.1	5203.0
30.0	-43.5	-38.4	1.00E6	5237.8	4151.5
50.0	-45.4	-34.7	1.00E6	4415.2	3057.2
70.0	-46.5	-32.3	1.00E6	3999.4	2528.3
80.0	-46.9	-31.3	1.00E6	3860.8	2347.5
100.0	-47.5	-29.8	1.00E6	3659.2	2095.6
200.0	-49.0	-25.2	1.00E6	3210.5	1510.7
400.0	-50.4	-22.0	1.00E6	2800.1	1131.4
600.0	-51.2	-20.5	1.00E6	2579.7	964.6
800.0	-51.8	-19.7	1.00E6	2419.9	866.5
1000.0	-52.2	-19.1	1.00E6	2319.6	803.2
2000.0	-53.3	-17.4	1.00E6	2063.7	646.7
4000.0	-54.4	-15.7	1.00E6	1834.4	515.7
7000.0	-55.2	-14.1	1.00E6	1685.4	423.3
10000.0	-55.7	-13.0	1.00E6	1598.5	369.1
20000.0	-56.4	-10.2	1.00E6	1489.6	268.0
30000.0	-56.7	-8.6	1.00E6	1445.8	218.6
50000.0	-57.0	-6.3	1.00E6	1404.0	155.0
70000.0	-57.1	-4.7	1.00E6	1391.7	114.4
90000.0	-57.1	-3.3	1.00E6	1394.1	80.4
100000.0	-57.1	-2.9	1.00E6	1394.6	70.7
100000.0	-51.6	-12.2	5.00E5	1285.4	277.9
200000.0	-51.7	-16.6	5.00E5	1245.9	371.4
300000.0	-51.7	-22.6	5.00E5	1200.3	499.6
500000.0	-51.9	-40.3	5.00E5	969.0	821.7
700000.0	-53.0	-62.7	5.00E5	513.4	994.7
900000.0	-54.7	-80.4	5.00E5	153.5	907.5
1000000.0	-55.6	-88.7	5.00E5	18.8	829.6

* These measurements were done with Lissajous figures.

Table 5.30 Real and Imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 723 K

Freq (Hz)	B/A(dB)	ϕ (deg)	R_s	Z' (ohms)	$-Z''$ (ohms)
*					
0.004				1023369.0	527327.0
0.006				884399.0	523709.0
0.008				808833.7	519816.0
0.009				645116.9	449549.9
0.01				612865.9	446806.3
0.02				500269.0	404107.5
0.03				411833.5	364723.4
0.05				328469.8	320361.9
0.06				297436.3	305683.3
0.08				283378.0	291940.1
0.1				236872.6	257959.7
0.5				94956.7	110066.9
0.7				81332.3	97570.4
0.9				65543.6	79030.6
1.0	-35.7	-55.8	4500000.0	41030.4	62191.2
1.5	-37.8	-56.0	4500000.0	32128.5	48754.9
2.0	-39.2	-55.7	4500000.0	27602.6	41266.6
3.0	-41.2	-54.2	4500000.0	22816.0	32112.0
3.0	-38.3	-55.2	3000000.0	20663.8	30378.0
4.0	-39.5	-54.6	3000000.0	18294.1	26221.6
5.0	-41.0	-52.4	3000000.0	16251.6	21415.3
5.0	-37.3	-52.7	2000000.0	16435.6	22070.7
6.0	-38.1	-53.4	2000000.0	14747.7	20279.6
7.0	-38.9	-52.2	2000000.0	13846.5	18187.5
8.0	-39.6	-51.8	2000000.0	12897.4	16671.3
9.0	-40.0	-51.6	2000000.0	12375.6	15869.4
10.0	-40.4	-51.3	2000000.0	11900.7	15085.4
20.0	-44.0	-51.0	2000000.0	7924.6	9885.2
30.0	-45.7	-48.6	2000000.0	6854.8	7836.8
30.0	-40.1	-48.3	1000000.0	6564.0	7478.6
40.0	-41.5	-47.6	1000000.0	5666.8	6284.3
50.0	-42.4	-46.7	1000000.0	5198.5	5578.5
60.0	-43.4	-44.8	1000000.0	4797.6	4810.0

Contd..

70.0	-43.9	-45.3	1000000.0	4488.7	4577.8
80.0	-44.5	-44.8	1000000.0	4226.9	4233.0
90.0	-45.0	-44.3	1000000.0	4025.3	3959.3
100.0	-45.5	-43.8	1000000.0	3832.7	3702.7
200.0	-48.3	-40.6	1000000.0	2922.4	2517.4
400.0	-50.9	-37.3	1000000.0	2270.1	1735.6
400.0	-45.1	-36.4	500000.0	2241.7	1664.3
500.0	-45.9	-35.4	500000.0	2070.5	1480.7
700.0	-47.1	-33.8	500000.0	1838.4	1237.2
900.0	-47.8	-32.6	500000.0	1719.5	1105.0
1000.0	-48.1	-32.1	500000.0	1670.3	1052.6
2000.0	-50.0	-27.8	500000.0	1401.5	741.5
3000.0	-51.1	-25.0	500000.0	1265.0	591.7
5000.0	-52.2	-21.3	500000.0	1145.7	447.9
7000.0	-52.8	-19.0	500000.0	1085.1	374.5
9000.0	-53.2	-17.4	500000.0	1045.8	328.5
10000.0	-53.3	-16.8	500000.0	1037.2	313.8
10000.0	-53.2	-16.6	500000.0	1050.3	313.8
20000.0	-54.0	-12.8	500000.0	974.6	221.9
30000.0	-54.3	-11.2	500000.0	947.1	187.9
50000.0	-54.7	-9.5	500000.0	909.4	152.5
70000.0	-54.9	-8.6	500000.0	890.9	135.0
90000.0	-55.0	-8.0	500000.0	882.0	124.2
100000.0	-55.1	-8.0	500000.0	871.9	122.7
200000.0	-55.0	-7.2	500000.0	883.7	111.8
300000.0	-54.5	-8.8	500000.0	932.4	144.7
400000.0	-53.8	-12.8	500000.0	997.4	227.1
600000.0	-53.0	-27.2	500000.0	997.0	513.7
800000.0	-53.1	-47.7	500000.0	744.5	820.9
1000000.0	-54.1	-66.4	500000.0	393.5	905.2

Table 5.31 Real and Imaginary components of the impedance from the measurements on gain phase meter and Lissajous figures at 673K

Freq(Hz)	B/A(dB)	ϕ (deg)	R_s (Ω)	Z' (k Ω)	$-Z''$ (k Ω)
0.001		-25.7	20.0 E6	2511.8	1444.7
0.002		-30.4	20.0 E6	2238.4	1530.8
0.003		-34.1	20.0 E6	1932.0	1510.6
0.005		-37.7	20.0 E6	1618.9	1429.8
0.008		-40.2	20.0 E6	1346.9	1284.5
0.01		-44.6	20.0 E6	1153.6	1282.5
0.03		-50.2	20.0 E6	685.5	898.8
0.05		-50.5	20.0 E6	530.9	690.5
0.07		-52.4	20.0 E6	501.1	699.2
0.09		-53.6	20.0 E6	423.7	611.1
0.1		-54.5	20.0 E6	391.0	582.7
0.3		-59.4	20.0 E6	172.2	301.3
0.5		-57.0	20.0 E6	132.3	208.5
0.7		-50.3	20.0 E6	131.1	160.3
1.0	-27.2	-55.2	4.00 E6	96.7	150.6
2.0	-30.8	-55.4	4.00 E6	64.2	98.1
2.0	-28.4	-55.5	3.00 E6	62.9	98.1
3.0	-30.9	-55.8	3.00 E6	47.1	73.0
4.0	-32.5	-58.0	3.00 E6	36.9	61.8
4.0	-29.1	-55.4	2.00 E6	38.9	60.1
5.0	-30.1	-53.8	2.00 E6	36.3	52.3
6.0	-31.4	-53.5	2.00 E6	31.6	44.7
7.0	-29.5	-53.8	1.50 E6	29.1	42.2
8.0	-30.2	-53.9	1.50 E6	26.8	38.8
9.0	30.8	-53.3	1.50 E6	25.5	35.9
10.0	-31.7	-52.0	1.50 E6	23.7	31.7
20.0	-34.3	-54.7	1.50 E6	16.5	24.1
20.0	-31.7	-48.3	1.00 E6	17.2	20.1
30.0	-33.3	-48.1	1.00 E6	14.4	16.6
30.0	-27.6	-47.8	5.00 E5	13.9	16.3

Contd..

40.0	-28.8	-46.0	5.00 E5	12.6	13.7
50.0	-29.8	-44.9	5.00 E5	11.4	12.0
60.0	-30.7	-43.1	5.00 E5	10.7	10.4
70.0	-31.2	-43.4	5.00 E5	10.0	9.8
80.0	-31.7	-42.7	5.00 E5	9.6	9.2
90.0	-32.2	-42.2	5.00 E5	9.1	8.5
100.0	-32.6	-41.7	5.00 E5	8.8	8.1
100.0	-30.8	-41.6	4.00 E5	8.7	8.0
200.0	-33.7	-38.4	2.00 E5	3.3	2.7
200.0	-27.7	-37.7	2.00 E5	6.6	5.4
300.0	-29.1	-35.8	2.00 E5	5.8	4.3
400.0	-30.1	-34.2	2.00 E5	5.2	3.7
500.0	-30.9	-32.9	2.00 E5	4.9	3.3
600.0	-31.4	-31.7	2.00 E5	4.6	3.0
700.0	-31.9	-30.6	2.00 E5	4.4	2.7
800.0	-32.2	-29.6	2.00 E5	4.3	2.5
900.0	-32.9	-28.6	2.00 E5	4.0	2.3
1000.0	-33.1	-27.9	2.00 E5	4.0	2.2
2000.0	-34.6	-22.4	2.00 E5	3.5	1.5
3000.0	-35.3	-19.5	2.00 E5	3.3	1.2
4000.0	-35.7	-17.7	2.00 E5	3.2	1.0
5000.0	-35.9	-16.4	2.00 E5	3.1	0.9
6000.0	-36.1	-15.4	2.00 E5	3.1	0.9
7000.0	-36.3	-14.8	2.00 E5	3.0	0.8
9000.0	-36.5	-13.8	2.00 E5	2.9	0.7
10000.0	-36.7	-13.5	2.00 E5	2.9	0.7
20000.0	-37.2	-12.0	2.00 E5	2.7	0.6
30000.0	-37.5	-12.0	2.00 E5	2.6	0.6
40000.0	-37.6	-12.4	2.00 E5	2.6	0.6
50000.0	-37.7	-13.0	2.00 E5	2.6	0.6
70000.0	-37.9	-14.6	2.00 E5	2.5	0.7
90000.0	-38.0	-16.8	2.00 E5	2.4	0.7
100000.0	-38.1	-17.8	2.00 E5	2.4	0.8
200000.0	-38.4	-29.2	2.00 E5	2.1	1.2
300000.0	-38.8	-41.0	2.00 E5	1.7	1.5
300000.0	-38.7	-41.1	2.00 E5	1.8	1.6
400000.0	-39.3	-53.2	2.00 E5	1.3	1.8
500000.0	-39.9	-64.9	2.00 E5	0.8	1.8
700000.0	-41.4	-87.3	2.00 E5	0.1	1.7

Table 5.32 Real and imaginary components of the impedance from the measurements on the gain phase meter and Lissajous figures at 623 K

Freq(Hz)	B/A(dB)	ϕ (deg)	R_s (ohms)	Z' (ohms)	Z'' (ohms)
0.002	*	-38.4	80.0 E6	7089652	654655
0.003		-42.7	80.0 E6	5344249	5628245
0.004		-44.5	80.0 E6	3928316	4277694
0.005		-44.3	80.0 E6	3765741	4052346
0.006		-45.2	80.0 E6	3453828	3812474
0.007		-45.7	80.0 E6	3262434	3655665
0.008		-45.8	80.0 E6	3037980	3395706
0.009		-46.1	80.0 E6	2977883	3355992
0.01		-47.0	80.0 E6	2797073	3239530
0.02		-50.2	60.0 E6	1874858	2436804
0.04		-51.4	60.0 E6	1274919	1691376
0.05		-53.1	60.0 E6	1125079	1584039
0.06		-55.0	60.0 E6	965386.5	1452838
0.06		-52.2	40.0 E6	1001932	1387590
0.07		-54.5	40.0 E6	872765.1	1312054
0.08		-52.9	40.0 E6	837409.1	1177136
0.09		-52.2	40.0 E6	777459.0	1057435
0.1		-53.4	40.0 E6	708764.2	1004515
0.2		-55.4	40.0 E6	453512.7	682793.9
0.3		-58.2	40.0 E6	330188.9	549325.6
0.4		-53.1	40.0 E6	331422.9	452392.5
0.5		-55.9	40.0 E6	256629.3	386271.6
0.7		-53.1	40.0 E6	237180.3	321570.9
0.9		-45.6	40.0 E6	233417.7	241074.0
1.0	-42.1	-55.0	40.0 E6	179285.4	259613.6
2.0	-45.8	-52.6	40.0 E6	124315.9	163991.0
3.0	-47.7	-50.9	40.0 E6	103818.6	128591.5
5.0	-50.4	-48.5	40.0 E6	79995.1	90835.9
7.0	-51.8	-46.8	40.0 E6	70367.6	75211.1
10.0	-52.9	-40.9	40.0 E6	68499.1	59512.1

Contd..

20.0	-55.8	-37.9	40.0 E6	51214.1	39950.5
30.0	-58.3	-38.5	40.0 E6	38084.4	30340.6
50.0	-59.7	-39.3	40.0 E6	32050.9	26266.8
70.0	-61.4	-37.6	40.0 E6	26981.6	20801.5
100.0	-62.9	-36.4	40.0 E6	23062.2	17019.3
200.0	-65.2	-30.9	40.0 E6	18868.0	11299.3
400.0	-64.0	-25.7	30.0 E6	17063.4	8217.9
600.0	-64.8	-22.4	30.0 E6	15967.9	6585.0
800.0	-55.6	-17.7	10.0 E6	15832.3	5061.4
1000.0	-56.2	-16.0	10.0 E6	14908.3	4281.8
2000.0	-57.3	-10.8	10.0 E6	13421.6	2563.8
3000.0	-57.9	-7.5	10.0 E6	12641.9	1666.8
5000.0	-50.7	-14.6	4.00 E6	11322.7	2958.3
6000.0	-50.7	-14.9	4.00 E6	11306.9	3017.8
7000.0	-50.8	-15.3	4.00 E6	11155.7	3060.9
8000.0	-50.7	-15.8	4.00 E6	11257.9	3195.3
10000.0	-50.7	-16.9	4.00 E6	11193.8	3411.5
20000.0	-51.2	-24.1	4.00 E6	10077.0	4521.2
40000.0	-52.3	-39.9	4.00 E6	7450.0	6249.7
60000.0	-53.9	-53.7	4.00 E6	4774.9	6522.0
80000.0	-56.1	-64.6	4.00 E6	2682.0	5668.7
100000.0	-58.7	-71.9	4.00 E6	1438.9	4419.0
150000.0	-66.0	-65.5	4.00 E6	830.7	1825.0
200000.0	-68.1	-27.5	4.00 E6	1396.7	727.4
300000.0	-63.5	-12.2	4.00 E6	2614.6	565.6
500000.0	-61.0	-34.4	4.00 E6	2942.8	2017.0
700000.0	-61.1	-57.8	4.00 E6	1876.7	2984.9
900000.0	-61.8	-79.1	4.00 E6	612.3	3193.6
1000000.0	-62.4	-88.8	4.00 E6	61.2	3033.7

* These measurements were made with Lissajous figures.

Table 5.33 Real and imaginary components of the impedance from the measurements on the gain phase meter and Lissajou figures for the dummy sensor

Freq	A	B	ϕ	R_s	Z'	Z''
Hz	dB	dB	deg	ohms	ohms	ohms
0.01			-1.6	10.00 E6	470932	13715
0.05			-8.2	10.00 E6	471113	71250
0.1			-16.2	10.00 E6	435120	132837
0.5			-55.5	10.00 E6	139258	211870
1.0			-68.5	10.00 E6	51156	135398
1.0	6.4	-30.4	-72.1	10.00 E6	42710	138752
2.0	11.2	-31.3	-80.5	10.00 E6	11842	74139
5.0	11.2	-39.2	-85.9	10.00 E6	2068	30135
5.0	11.2	-29.6	-85.7	3.50 E6	2104	31872
10.0	11.2	-35.7	-87.7	3.50 E6	563.6	15808
10.0	11.2	-30.8	-87.5	2.00 E6	567.5	15881
20.0	11.2	-30.7	-88.4	1.00 E6	159.6	8035
50.0	17.2	-32.5	-89.1	1.00 E6	40.6	3273
100.0	17.2	-38.5	-89.3	1.00 E6	17.3	1640.6
100.0	17.2	-32.6	-89.2	5.00 E5	17.4	1617.9
500.0	17.2	-46.7	-88.7	5.00 E5	7.0	319.1
500.0	23.2	-40.4	-88.7	5.00 E5	7.3	330.3
1000	23.2	-46.5	-88.0	5.00 E5	5.7	163.6
1000	23.2	-38.5	-87.7	2.00 E5	6.5	164.3
10000	23.2	-58.1	-89.7	2.00 E5	0.1	17.2
20000	23.2	-31.3	-75.4	5000.0	2.4	9.1
50000	23.2	-37.9	-60.5	5000.0	2.2	3.8
100000	23.2	-42.6	-44.4	5000.0	1.8	1.8

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