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Strong temperature dependence of oxygen diffusion through porous platinum

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Abstract—The diffusion of nitrogen, oxygen and argon gas through a porous platinum sample was experimentally investigated. Unlike nitrogen and argon gas the diffusion flow rate of oxygen gas shows a strong temperature dependence in the temperature range considered (300–1000 K). The diffusion flow rate of oxygen decreases with increasing sample temperature. The observed effect is explained by ozone formation and back diffusion which reduces the total oxygen mass (oxygen and ozone) diffusion flow rate. Ozone is formed inside the porous platinum sample. © 1997 Elsevier Science Ltd.

INTRODUCTION

During the course of experiments dealing with the diffusion of gas through porous platinum, performed with the purpose to cover the surface of the porous body with adsorbate, it was observed that oxygen gas diffusion flow rate shows a strong temperature dependence if compared with the diffusion flow rate of nitrogen or argon gas through the porous platinum sample in the same temperature range (300–1000 K). The oxygen diffusion flow rate at 1000 K sample temperature was only ≈1/3 of the diffusion flow rate at 300 K sample temperature. The gas transport through the pores occurs in the Knudsen regime and the temperature dependence of the diffusion flow rate is expected to show the temperature dependence of the Knudsen diffusion coefficient [1]. This could be observed in the case of nitrogen and argon gas, but not in the case of oxygen diffusion through porous platinum. The observed effect is explained by back diffusion of ozone formed inside the porous platinum sample, which reduces the total oxygen mass (oxygen and ozone) diffusion flow. The observed effect can be used for the design of devices which separate oxygen gas from gas mixtures.

EXPERIMENTAL

In Fig. 1 the experimental set-up for the diffusion of oxygen, nitrogen and argon gas through the porous platinum sample is shown. The cylindrical porous platinum sample (diameter: 8 mm, height: 8 mm) is made of small platinum spheres (diameter of the platinum spheres ≈60 μm, diameter of the pores ≈22 μm). One side of the sample was 2 mm pressed into a thin-walled platinum tube. The other side of the sample was covered by a platinum sheet that was connected to a resistance heater. All platinum components are made of 99.999% platinum. The sample is placed in a ultra-high-vacuum apparatus (base pressure 10^{-7} Pa) which consists of two chambers (I, II) connected by the platinum tube with the sample. The two chambers are equipped with turbomolecular pumps. The pumping speeds (indicated in Fig. 1) were kept constant during the measurements. Chamber (I) is equipped with gas inlet valves. High purity gas admitted to chamber (I) arrives at chamber (II) by diffusion through the porous platinum sample. The pressure of high purity oxygen, nitrogen and argon gas in chamber (I) and (II) was measured with ionization gauges calibrated for each gas by a friction vacuum meter in a pressure regime overlapping with the ionization gauge. Chamber (I) and chamber (II) was at room temperature (≈295 K) during all the experiments. Partial pressure of selected gases in chamber (II) was measured with a quadropole mass spectrometer (QMS) in counting rates. Counting rates and partial pressures are proportional and it was measured that $1 \cdot 10^{-7}$ Pa gas pressure of nitrogen molecules, oxygen molecules or argon atoms corresponds to counting rates of $2.56 \cdot 10^4$ Hz, $2.08 \cdot 10^4$ Hz and $1.64 \cdot 10^4$ Hz. The axis of the quadropole points normal to the cylinder surface of the sample with the ion source close by the sample (25 mm). The quadropole mass spectrometer and an ion gun for argon and xenon were used for secondary ion mass spectroscopy (SIMS) measurements on the surface of the porous platinum sample. The sample temperature was measured with three thermocouples attached to the sample and positioned along a line parallel to the cylinder axis. The porous platinum sample was cleaned *in situ* by cycles of heating to 950 K with oxygen diffusing through the sample and heating to the same temperature under UHV conditions. The oxygen pressure in chamber (I) was raised to $1 \cdot 10^{-4}$ Pa during heating with oxygen exposure. SIMS measurements were performed to check the cleanliness of the sample. Calcium and aluminum impurities were detected on the surface

NOMENCLATURE

T_I	temperature in chamber (I)
T_S	temperature of the porous platinum sample
N_S	number density of gas particles in the first pores
N_I	number density of the gas particles in chamber (I)
j	total oxygen mass diffusion flow rate (O_2 as well as O_3 mass)
O_2	oxygen
O_3	ozone
C_{O_2}	oxygen concentration
C_{O_3}	ozone concentration
$[O_2]$	oxygen concentration in thermodynamic equilibrium
$[O_3]$	ozone concentration in thermodynamic equilibrium
d_{O_2}	oxygen diffusion constant
d_{O_3}	ozone diffusion constant
x_1	position along the line in the one-dimensional model
x_2	position along the line in the one-dimensional model.
Greek symbols	
η	proportionality constant which relates in thermodynamic equilibrium the oxygen and the ozone concentration.
Subscripts	
I	chamber (I)
S	porous platinum sample
O_2	oxygen
O_3	ozone.

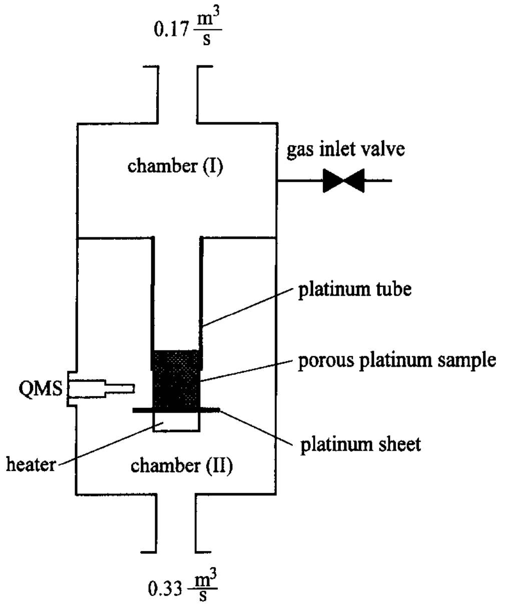

Fig. 1. Schematic description of the experimental setup for diffusion experiments. Vacuum chamber (I) and (II) are separated by a porous platinum sample. The sample is connected with a heating device. Partial pressures in chamber (II) were measured with a quadropole mass spectrometer (QMS). The vacuum chambers are equipped with turbomolecular pumps, the pumping speeds are indicated.

of the sample. The calcium impurity concentration was estimated to be lower than 0.2% and the aluminium impurity concentration lower than 0.02%.

RESULTS AND DISCUSSION

Diffusion experiments were performed under steady state conditions with constant total pressure in chamber (I) and a different temperatures of the porous platinum sample. The reported temperatures were measured by a thermocouple attached to the sample in a distance of 2.8 mm from the platinum sheet. Starting from room temperature the temperature of the sample was stepwise increased until approximately 1000 K was reached. At every temperature step, but more than 15 min after the sample has reached the new temperature, in order to secure steady state conditions, the partial pressure of the selected gas in chamber (II) was measured. The total pressure in chamber (I) and, therefore, the total pressure in chamber (II) was chosen low enough to make sure that the ion detector of the QMS was not in saturation.

The diffusion experiments were performed with argon, nitrogen and oxygen gas at total pressures lower than $1 \cdot 10^{-2}$ Pa in chamber (I) from which a mean free path of greater than 0.5 m can be calculated for each gas.

Figure 2 shows the results of diffusion experiments with nitrogen gas admitted into chamber (I). The QMS signals for mass 28 measured at constant total pressure in chamber (I) ($4.4 \cdot 10^{-3}$ Pa) and at different sample temperatures are shown. Similar experiments were performed with argon gas ($5.5 \cdot 10^{-3}$ Pa), whose results are shown in Fig. 3. In both cases (mass 28 and mass 40) no temperature dependence of the measured QMS signal was observed.

The observations can be explained if molecular flow conditions exists in chamber (I) and inside the pores of the porous platinum sample. The gas density in chamber (I) is low enough to have molecular flow conditions (Knudsen number greater than 2) and due to the small diameters of the pores of the porous sample the Knudsen number inside the sample is greater than 10^4, which also means molecular flow. In this case the exchange of gas between chamber (I) and the first pore volumes of the sample [first pores are

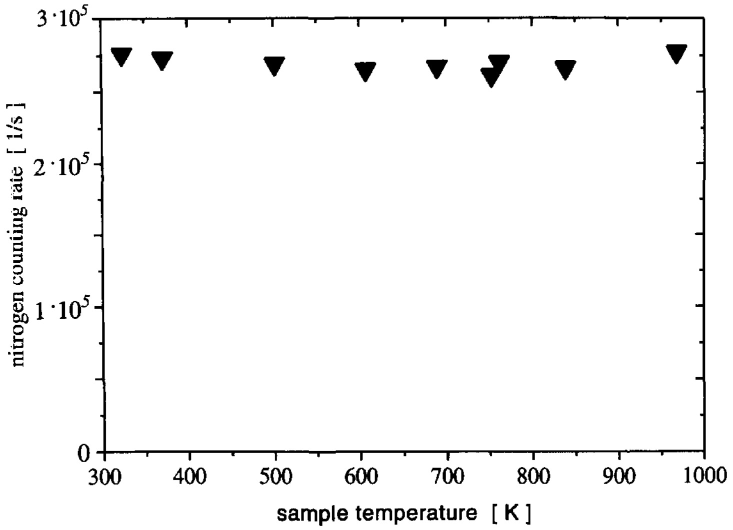

Fig. 2. Diffusion of nitrogen gas (mass 28) through the porous platinum sample as function of the sample temperature. The nitrogen partial pressure in chamber (II) is measured in ion counting rates. Total pressure in chamber (I) $4.4 \cdot 10^{-3}$ Pa.

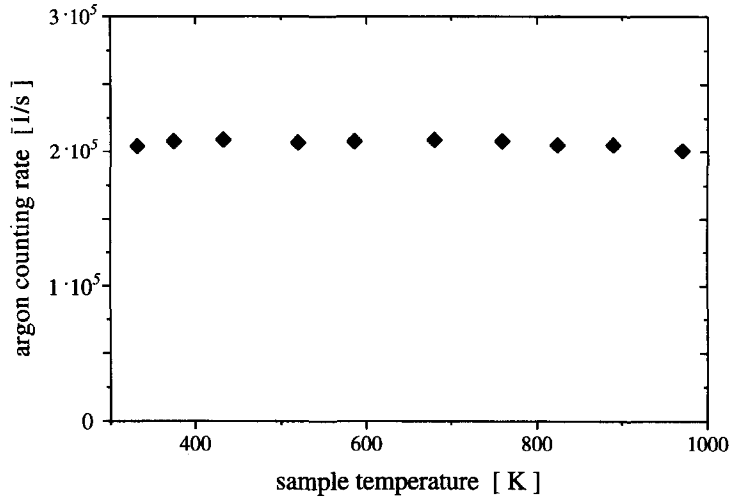

Fig. 3. Argon (mass 40) diffusion through the porous platinum sample. The argon partial pressure in chamber (II) measured in ion counting rates as function of the sample temperature is shown. The total pressure in chamber (I) during the experiment was $5.5 \cdot 10^{-3}$ Pa.

pores close to the surface with a small opening into chamber (I)] takes place by molecular flow. In equilibrium the number density of the particles of a certain gas in chamber (I) is, therefore, related to the number density of the same gas in the first pores by the temperature in chamber (I) T_I and the sample temperature T_S according to $N_S \cdot \sqrt{T_S} = N_I \cdot \sqrt{T_I}$ [N_S: = number density of gas particles in the first pores, N_I: = number density of the gas particles in chamber (I)] [2]. These arguments in combination with the assumption that back streaming of gas from chamber (II) into the pores of the porous sample can be neglected, due to the low pressure ($< 10^{-5}$ Pa) in chamber (II), the gas flow rate through the sample should be independent of the sample temperature, because the $1/\sqrt{T_S}$ temperature dependence of the gas particle number density in the first pores is compensated by the $\sqrt{T_S}$ proportionality of the Knudsen diffusion coefficient [1]. Due to the constant pumping speed in the chamber (II) the gas flow rate through the porous platinum sample is proportional to the gas pressure in chamber (II), which can be studied for the different gas species if partial pressures has been measured. In contrast to the diffusion experiments with nitrogen or argon gas a similar experiment performed with oxygen gas [total pressure in chamber (I) : $8.2 \cdot 10^{-3}$ Pa] shows a strong temperature dependence of the oxygen diffusion flow rate through the porous platinum. In Fig. 4 the results of the oxygen diffusion experiments are shown. At ≈ 700 K the mass 32 QMS signal (oxygen) starts to decline and continues to decline with increasing temperature. At ≈ 1000 K sample temperature only $\approx 1/3$

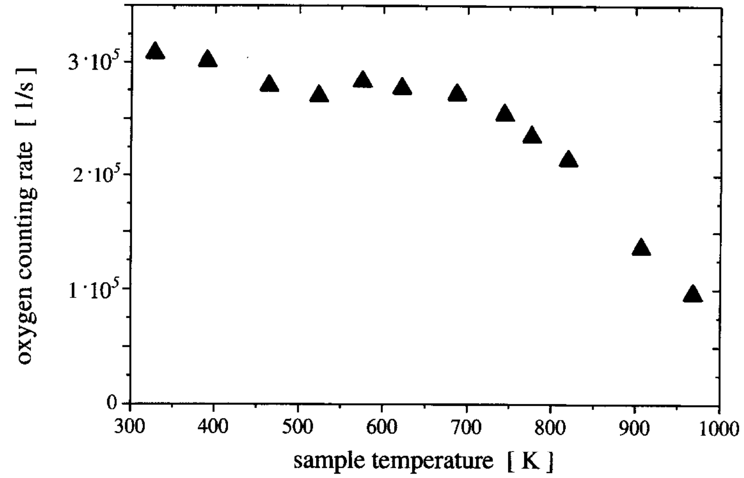

Fig. 4. Oxygen (mass 32) diffusion through porous platinum. The oxygen partial pressure in chamber (II) measured in ion counting rates as function of the sample temperature shows a strong temperature dependence. Total pressure in chamber (I) $8.2 \cdot 10^{-3}$ Pa.

of the mass 32 QMS signal detected at ≈300 K sample temperature is observed.

The strong temperature dependence of the oxygen diffusion flow rate should also be detectable with total gas pressure measurements under steady state conditions. Respective experiments were performed at constant sample temperature while the total gas pressure in chamber (I) was stepwise increased by adding oxygen gas. Three sample temperatures were selected 316, 611 and 959 K. The results are shown in Fig. 5. Total pressures in chamber (II) are linearly related to the total pressures in chamber (I), but show different slopes at the three selected sample temperatures. The slope should be proportional to the oxygen diffusion flow rate through the porous platinum sample and, therefore, it can be concluded that the diffusion flow rate of oxygen at 959 K sample temperature is only ≈1/3 of the diffusion flow rate at 316 K, which is in agreement with the partial gas pressure measurements mentioned above (Fig. 4). The clear offset in total pressure ($\approx 4 \cdot 10^{-7}$ Pa) observed in the experiment with 959 K sample temperature, if compared with the experiments performed at the lower sample temperatures, is explained by an increased base pressure due to outgassing of the sample holder during strong heating of the sample.

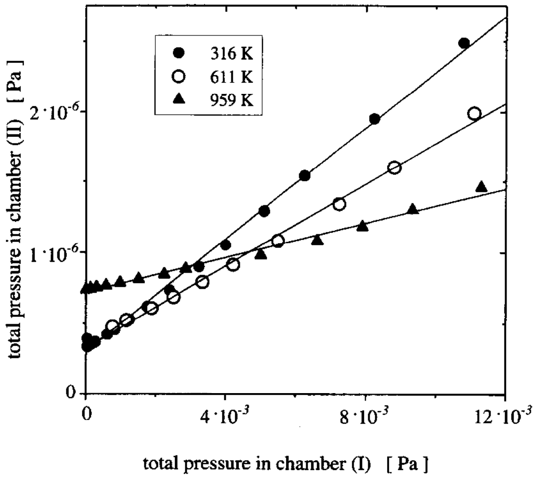

Fig. 5. Oxygen diffusion through porous platinum at three different sample temperatures 316, 611 and 959 K. The total gas pressure in chamber (I) was changed by adding oxygen gas. The total pressure in chamber (II) is shown as function of the total pressure in chamber (I). The cut of the curves with the ordinate is a measure of the background pressure in chamber (II).

How can we account for the observations? Ozone could be formed at elevated temperatures of the sample. This was checked in the oxygen diffusion experiment with constant total pressure in chamber (I) ($8.2 \cdot 10^{-3}$ Pa) mentioned above, where also the ozone QMS signal was recorded. The results are shown in Fig. 6. Although at ≈700 K sample temperature the mass 48 QMS signal (ozone) starts to increase strongly with increasing sample temperature, the ozone flow rate can not compensate the strong mass 32 QMS signal decrease, because the mass 48 signal at 950 K sample temperature is more than one order of magnitude lower than the mass 32 signal difference between 300 and 950 K sample temperature, unless the QMS is much more sensitive for O_2 than for O_3 molecules, but this is not expected because the experimental results with total gas pressure measurements in chamber (I) (Fig. 5) would point against such an interpretation. The mass 48 QMS counting rate is expected to be proportional to the ozone gas pressure in chamber (I), but, unfortunately, the constant of proportionality could not be determined, out of experimental reasons.

The oxidation of platinum could be responsible for the observed effect, if the formation of non volatile platinum oxides reduces the oxygen passage through the porous platinum sample [4]. To check this the

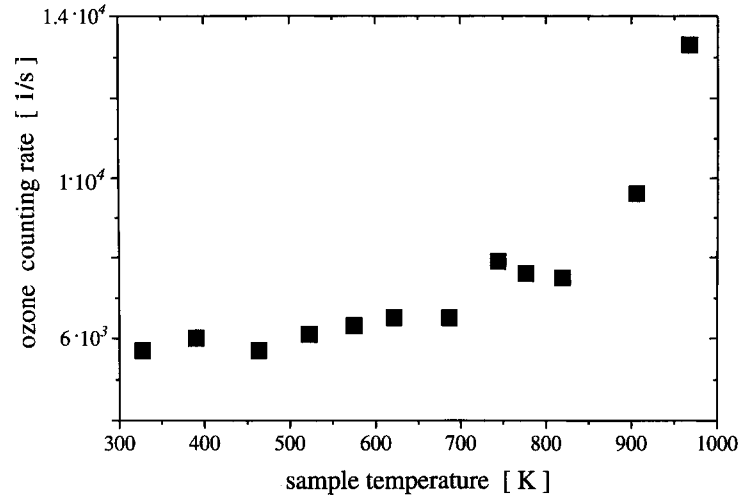

Fig. 6. Ozone (mass 48) partial pressure measured in ion counting rates in chamber (II) as function of the temperature of the porous platinum sample. Oxygen gas was admitted into chamber (I). Constant total pressure in chamber (I) $8.2\cdot 10^{-3}$ Pa.

platinum sample was heavily exposed to oxygen at ≈980 K (gas pressure in chamber (I): $5\cdot 10^{-2}$ Pa, exposure time: ≈ 50 h and it was investigated whether changes in the diffusion flow rate could be related to saturation effects due to the formation of non-volatile platinum oxides, but no changes in the diffusion flow rate could be observed, so the formation of non-volatile platinum oxides seems to be improbable for an explanation of the strong temperature dependence of oxygen diffusion flow rate through the porous platinum sample.

It was also investigated whether volatile platinum oxides must be considered to explain the observed effect [5]. To check this the porous platinum sample was again heavily exposed to oxygen ($5\cdot 10^{-2}$ Pa, ≈50 h) at 980 K sample temperature and a polished copper plate was placed 10 mm in front of the sample so that volatile platinum oxides should be deposited on the surface of the copper plate. After exposure the copper plate was analysed with SIMS [3], but no platinum or platinum oxides could be detected. So volatile platinum oxides seems not to be involved in the transport of oxygen through the porous platinum sample.

To have some information about the gas concentrations inside the porous platinum sample, outgassing experiments were performed. For this, the sample temperature was increased by ≈70 K with ≈ 0.7 K/s heating rate, starting at different sample temperatures with oxygen exposure via chamber (I) and constant total pressure in chamber (I) ($4\cdot 10^{-3}$ Pa). During the increase of the sample temperature the partial pressure increase of oxygen (mass 32) and ozone (mass 48) shows a pressure peak in chamber (II). The pressure increase peak heights are related to the gas concentrations in the sample pores and the absorbate coverage on the platinum surface (mainly the surface inside the sample) as function of the starting temperature. In Figs. 7 and 8 the outgassing partial pressure increase peak heights for oxygen and ozone, measured in counting rates, and normalized to the heating rate are shown. The ozone signal is observed to be approximately two orders of magnitude lower than the oxygen signal at 950 K sample temperature, if we assume that the sensitivity of the QMS for ozone an oxygen (mass 32) is the same. In addition the sample temperature dependencies are observed to be different. The oxygen signals show a maximum at 850 K sample temperature whereas the ozone signal only increases with sample temperature in the temperature range studied.

The reported experimental results raise the question whether ozone formation inside the sintered platinum sample is responsible for the observed strong temperature dependence of the oxygen diffusion. It is expected, because of the high Knudsen number ($>10^4$) for the gas inside the platinum sample, that reactions between the gas particles occur mainly on the surface of the small platinum spheres. From literature it is known, that ozone is formed at incandescent platinum surfaces exposed by oxygen gas [6] and, in addition, it is also known from literature, that ozone molecules are decomposed on this surface [7]. Ozone formation or decomposition seems to be controlled by the oxygen exposure of the incandescent platinum surface. Therefore, strong oxygen exposure with a relative high oxygen coverage on the platinum surface favours ozone formation, whereas on the same surface with low oxygen coverage mainly ozone decomposition is expected to occur. In this connection the boundary region of the sintered platinum sample, this is the several platinum spheres diameter thick transition region between the sintered platinum sample and the vacuum in chamber (II), must be distinguished in a theoretical description of the diffusion process from the description inside the sample. Ozone decomposition is expected to be the dominant process in the boundary region because of the relative low oxygen coverage on the platinum surface in this region

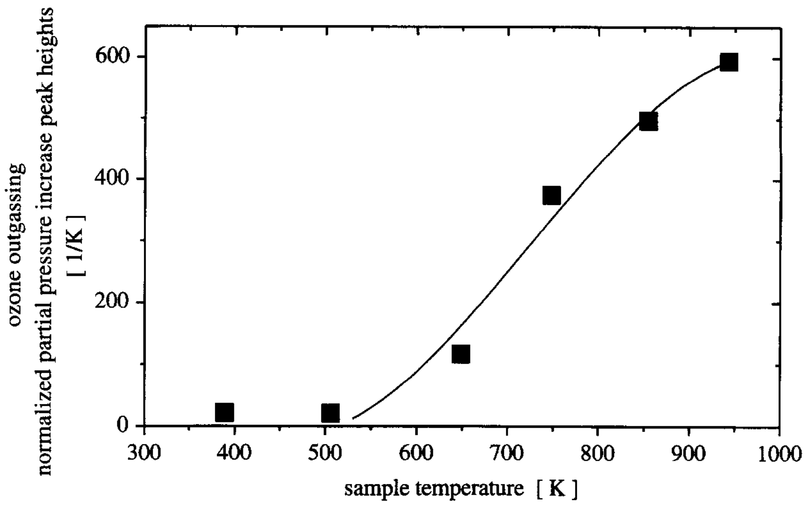

Fig. 7. Ozone (mass 48) outgassing partial pressure increase peak heights measured in ion counting rates and normalized to the heating rates are shown as a function of the temperature of the porous platinum sample. The fit is for illustration.

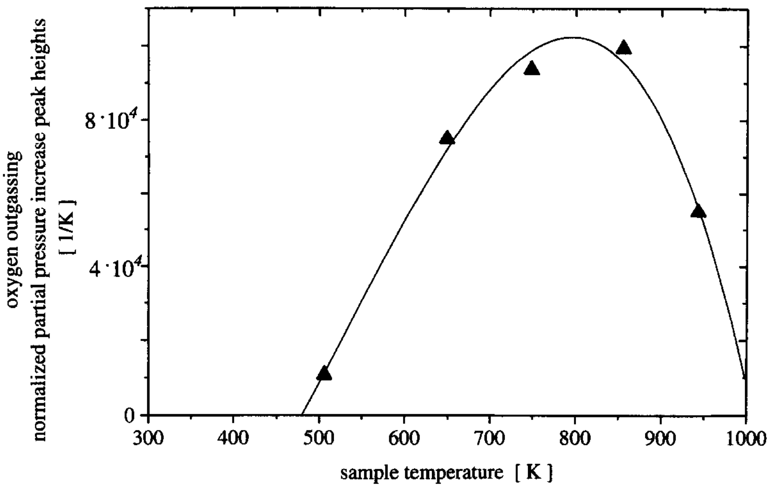

Fig. 8. Oxygen (mass 32) outgassing partial pressure increase peak heights measured in ion counting rates and normalized to the heating rates are shown as a function of the temperature of the porous platinum sample. The fit is for illustration.

due to desorption of oxygen adsorbates into chamber (II).

In a first approximation the diffusion through the cylindrical sample will be described in a one dimensional model with boundary condition described by the conditions in chamber (I) and (II). In this model only diffusion flow through a section between the boundaries will be discussed. This is sufficient for the calculation of the total oxygen mass diffusion flow rate (O_2 as well as O_3 mass) under steady state conditions because of the conservation of mass.

In the model, only diffusion flow is considered. Convective contributions to the oxygen flow through the porous platinum sample can be neglected because of the high Knudsen numbers inside the sample, which means that the oxygen molecules change their momentum nearly only by absorption/desorption processes on the platinum surface inside the sample. The desorption process is expected to be independent of the adsorption process, so that any convection is stopped.

With the assumption, that the rate by which the oxygen concentration C_{O_2} changes to achieve its thermodynamic equilibrium concentration in relation to the ozone concentration C_{O_3} is proportional to $1 - C_{O_3}/\eta \cdot C_{O_2}$, where η is a proportionality constant which relates in thermodynamic equilibrium the oxygen (O_2) and the ozone (O_3) concentrations (law of mass action, $[O_3] = \eta \cdot [O_2]$), it can be shown that the total oxygen mass diffusion flow rate j (oxygen and ozone) is given by

$$j = -d_{O_2} \cdot \frac{C_{O_2}(x_2) - C_{O_2}(x_1)}{x_2 - x_1} - d_{O_3} \cdot \frac{C_{O_3}(x_2) - C_{O_3}(x_1)}{x_2 - x_1}$$

where $C_{O_2}(x)$, $C_{O_3}(x)$ with $x = x_1$, x_2 ($x_1 < x_2$) are the O_2 and O_3 concentrations at the boundaries of the section at the positions x_1 and x_2 along the line in the one dimensional model and d_{O_2}, d_{O_3} are diffusion constants of oxygen and ozone, respectively. If a section can be found with $C_{O_3}(x_2) > C_{O_3}(x_1)$ and $C_{O_2}(x_2) < C_{O_2}(x_1)$ then ozone back diffusion can reduce the total oxygen mass diffusion flow rate is this model.

The observed low ozone concentration in chamber (II), which is at 950 K sample temperature approximately two orders of magnitude lower than the oxygen (O_2) concentration as mentioned above, seems to contradict this explanation, but it is expected, based on the arguments mentioned above, that ozone is decomposed into oxygen when passing the boundary region. So that the observed ozone/oxygen concentration relation in chamber (II) must not be in accordance with the ozone/oxygen concentration relation several platinum spheres diameter deep inside the sample.

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