# *Optimization of a Knudsen diffusion set-up for stable isotope research*

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### Abstract

Gas-phase diffusion is a widespread process in nature, for example diffusion of pollutants in the atmosphere. A special case of diffusion is the so-called Knudsen diffusion where a gas diffuses in the molecular flow regime. The theory for Knudsen diffusion is well-known therefore, diffusion experiments might be used to calibrate a new high-resolution gas source mass spectrometer.

This type of diffusion occurs when the mean free path length of the molecules is larger than the holes it diffuses through.

The question that will be answered in this thesis is: How does diffusion in the molecular flow regime change the isotopic composition of a gas? To study this research question experimentally, a diffusion set-up was used. The diffusion set-up is designed for investigating Knudsen diffusion.

Subsequent to optimizing the diffusion set-up, fractionation factors and  $\lambda$  values at a mean free path length of 726 µm were obtained. For the residue samples, the fractionation factors obtained were: 1000 ln (<sup>34</sup> $\alpha$ ) = (-31.7 ±1.7 (SE·t<sub>0.95</sub>))‰ and 1000 ln (<sup>33</sup> $\alpha$ )= (-15.8 ±0.6 (SE·t<sub>0.95</sub>)) ‰. The  $\lambda$  value, derived from these results is 0.50±0.01(SE·t<sub>0.95</sub>). On the diffused side the following fractionation factors were obtained: 1000 ln (<sup>34</sup> $\alpha$ ) = (-29.3 ±2.6(SE·t<sub>0.95</sub>))‰ and 1000 ln (<sup>33</sup> $\alpha$ )= (-15.7 ±0.7(SE·t<sub>0.95</sub>)) ‰. The corresponding  $\lambda$  value is: 0.533 ± 0.05(SE·t<sub>0.95</sub>). The measured flow rate is (0.225 ±0.08) (SE·t<sub>0.95</sub>) mL/h for 100 holes.

Diffused gas samples (mL amounts) can be prepared in 1.5h for mass spectrometric calibration purposes. The change in isotopic composition during Knudsen diffusion corresponds to the theoretical prediction (within a 1  $\sigma$  error), for both the residual- and diffused gas samples at a mean free path length of 726  $\mu$ m. Increasing the mean free path length resulted in fractionation factors closer to the predicted value. The reason is that the diffusion approaches a pure molecular flow regime at lower starting pressures (higher mean free path lengths). At lower mean free path lengths the occurring flow might be an intermediate of viscous and molecular flow.

The results have a large error in the calculated fraction of the gas. Decreasing this error would also result in a better estimation of the fractionation factors. For all mean free path lengths, the observed flow rate is about ten times lower than the expected flow rate. The reason for this deviation is unclear, it might be related to an erroneous estimate of the diameters of the holes.

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### **1** Introduction

The main constituents of atmospheric air are nitrogen (78%), oxygen (21%), water vapour (0.7%), argon (0.27%) and carbon dioxide (0.03%). The fate of these atmospheric gases and other trace gases in the atmosphere, biosphere and hydrosphere can be studied by investigating their isotopic composition. The isotopic composition describes the variation in mass of the gas. Carbon dioxide, for example, contains carbon with a molecular mass of 12 or 13 u and 2 oxygen molecules with a molecular mass of 16, 17 or 18 u. This variation in element weight is caused by the nucleus. The nucleus consists of protons and neutrons. Molecules with the same amount of protons but a different amount of neutrons have a different isotopic composition and are therefore termed isotopologues (see Sharp, 2007).

To study the atmosphere, samples can be taken from the atmosphere and analysed with a Gas Source-Isotope Ratio Mass Spectrometer (GS-IRMS). Due to the small variations in the abundance of the different isotopologues of a certain gas, it is important that these spectrometers are able to measure the smallest variations in the isotopologue abundance ratios.

In this bachelor thesis, the effect of Knudsen diffusion on the isotopic composition of stable isotopes will be investigated. Knudsen diffusion refers to diffusion of molecules through holes smaller than their mean free path length (Yeung, Young, & Schauble, 2012). To study gas flow in the molecular flow regime, the gas is diffusing from a low pressure side (0.05 to 0.2mbar) through small holes ( $\mu$ m scale) into high vacuum. Knudsen diffusion is chosen as it can be used to study clumped isotopes (i.e. molecules containing 2 heavy isotopes) (Eiler, 2007) as the underlying physical processes are well understood. This makes it possible to use the samples, obtained from the diffusion set-up, to calibrate mass spectrometric analyses.

Therefore, the main research question is how does diffusion in the molecular flow regime change the isotopic composition of a gas (e.g.  $O_2$ ,  $CO_2$ . and  $N_2O$ ). To answer this question it is important that the diffusion takes place in the molecular flow regime and not in the viscous flow regime. Therefore it is also important to study the flow rate.

Previous measurements were promising but very time-consuming (Linde, 2015). The results of previous measurements did correspond to theory. However, the reproducibility was low. These previous measurements were carried out with capillaries with a diameter of 75  $\mu$ m. The diffusion through these capillaries was very slow and the flow rate did not correspond to theory. The challenge is to improve the set-up, in a way that the experiments are highly reproducible and less time-consuming so that the diffused gas samples can be used to calibrate a new high-resolution gas source mass spectrometer (Eiler, et al., 2013) with the results.

In chapter two the underlying theory will be described account this is the diffusional flow rate, the abundance of the isotopes, and isotopic effects of Knudsen diffusion. Followed by the method section in which the experimental set-up, the stable isotope measurements and the error calculations will be discussed. Then, in the results section, the observed diffusional flow rate and the change in isotopic composition will be presented. The results will be compared to the predicted values in the discussion section.

### 2 Diffusion

#### 2.1 Molecular flow rate

In the diffusion set-up, the gas diffuses with a certain flow rate from a gas reservoir through a flow restriction, e.g. glass capillaries or a perforated aluminium foil. The experimentally determined flow rate will be compared to both the calculated molecular flow rate.

The flow rate is defined as the amount of gas (mL) that diffuses through the holes time unit. The flow rate is determined by the amount of molecules that pass an orifice. Which can be written as:

$$\frac{dN}{dt} = Z \cdot A \cdot t \cdot x = \frac{A \cdot p \cdot N_a}{\sqrt{2\pi \cdot M \cdot R \cdot T}} \cdot t \cdot x$$
(1) (Low-Pressure Effusion Of Gases, 2005)

with:

dN	diffused molecules	(-)
dt	time unit	(s)
t	time	(s)
X	amount of holes	(-)
Ζ	collision frequency	(s <sup>-1</sup> )
Α	area of an orifice	(m²)
R	ideal gas constant	(J/K mol)
N <sub>A</sub>	Avogadro's constant (6.022·10 <sup>23</sup> )	(mol⁻¹)
p	pressure in the set-up	(Pa)
Т	temperature in the set-up	(K)
М	molecular mass	(g/mol).

The determination of the collision frequency is illustrated in appendix B. Now the flow rate is determined in molecules that diffuse. When leaving Avogadro's constant out of the equation one can calculate the amount of moles *n* per second.

The amount of change in moles can be written as:

$dn = \frac{1}{R}$	$\frac{V}{VT}dp$		
Gases,	2005)		
with:			
dn	change in moles	(-	·)
V	volume of the set-up	()	n³)
dp	pressure drop	(1	۶a).

When substituting equation one in equation two:

 $\frac{dp}{p} = -\frac{A}{V} \sqrt{\frac{RT}{2\pi M}} = -\frac{dt}{\tau}$ Integrating results in:  $\int_{P_0}^p \frac{dp}{p} = \int_0^t -\frac{dt}{\tau} = \ln\left(\frac{p}{p_0}\right) = -\frac{t}{\tau}$ Gases, 2005) The pressure drop can now be written as:  $p = p_0 \cdot e^{\frac{-t}{\tau}}$ Gases, 2005)

(2) (Low-Pressure Effusion Of

(4) (Low-Pressure Effusion Of

(3) (Low-Pressure Effusion Of

In the molecular flow regime the flow rate is only determined by the random movement of the molecules, whereas in a viscous flow regime there is a continuous flow (see Figure 1) To following figure illustrates the principle of the various flows.



Figure 1. An overview of the possible flows is illustrated in this figure. From left to right: The viscous flow (continuous flow), A combination of the viscous and molecular flow and the molecular flow are shown. (Ideal Vacuum products, 2016)

To reach the molecular flow regime, the mean free path length of the molecules has to be larger than the size of the orifice it diffuses through. The ratio of the mean free path length and the orifice size is the so-called Knudsen number. When the flow rate is a molecular flow, the flow rate is independent of pressure, in that sense that the slope is constant (see Figure 2). The next plot illustrates equation 4. It shows that the flow rate is independent of the pressure. (Knudsen, 1933)



Figure 2. The pressure drop as a function of time (y-axis on logarithmic scale). The lines are plotted for 0.3, 0.2, and 0.1 millibar (i.e. 1.5, 1, and 0.5 mL).

#### 2.2 Oxygen and carbon isotope abundances and stable Isotope notation

Isotopes are defined as atoms with the same amount of protons, but vary in the amount of neutrons in their nuclei. In this bachelor thesis the kinetic fractionation of stable isotopes during diffusion will be investigated for  $CO_2$  and  $O_2$ . In contrast to radiogenic isotopes, stable isotopes are elements that do not decay (radioactively). Stable isotope analysis is used to identify sources, estimate reaction rates and infer processes.

Natural carbon dioxide consists of the stable carbon isotopes <sup>12</sup>C and <sup>13</sup>C and the stable oxygen isotopes <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O. The natural abundance level of <sup>12</sup>C and <sup>13</sup>C is 98.93% and 1.11%; the natural abundance level of <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O is 99.76%, 0.04% and 0.20% respectively. All combinations of carbon and oxygen isotopes in  $CO_2$  and their natural abundance levels are listed in Table 1. These molecules that differ only in their isotopic composition are also termed isotopologues.

Mass	Isotoplogue	Abundance
44	<sup>16</sup> O <sup>12</sup> C <sup>16</sup> O	98.93%
45	<sup>16</sup> O <sup>13</sup> C <sup>16</sup> O	1.11%
	<sup>17</sup> O <sup>12</sup> C <sup>16</sup> O	748 ppm
46	<sup>18</sup> O <sup>12</sup> C <sup>16</sup> O	0.40%
	<sup>17</sup> O <sup>13</sup> C <sup>16</sup> O	8.4 ppm
	<sup>17</sup> O <sup>12</sup> C <sup>17</sup> O	0.142 ppm
47	<sup>18</sup> O <sup>13</sup> C <sup>16</sup> O	44.4 ppm
	<sup>18</sup> 0 <sup>12</sup> C <sup>17</sup> 0	1.5 ppm
	<sup>17</sup> O <sup>13</sup> C <sup>17</sup> O	1.6 ppb
48	<sup>18</sup> O <sup>12</sup> C <sup>18</sup> O	3.96 ppm
	<sup>17</sup> O <sup>13</sup> C <sup>18</sup> O	16.8 ppb
49	<sup>18</sup> O <sup>13</sup> C <sup>18</sup> O	44.5 ppb

#### Table 1. Abundance of stable CO<sub>2</sub> isotopes.

The abundance of all possible oxygen isotopologues is illustrated in Table 2.

Mass	Isotopologue	Abundance
32	<sup>16</sup> O <sup>16</sup> O	99.5%
33	<sup>16</sup> 0 <sup>17</sup> 0	0.04%
34	<sup>16</sup> O <sup>18</sup> O	0.1995%
	<sup>17</sup> 0 <sup>17</sup> 0	0.15 ppm
35	<sup>17</sup> 0 <sup>18</sup> 0	1.6 ppm
36	<sup>18</sup> 0 <sup>18</sup> 0	4.2 ppm

#### Table 2. Abundance of stable O<sub>2</sub> isotopes.

When a molecule contains two heavy isotopes, like <sup>17</sup>O<sup>18</sup>O, it is called a doubly substituted or a clumped isotopologue. The term clumped isotopologue refers to the fact that thermodynamics predict that the two heavy isotopes will have the tendency to clump together at Earth surface temperature (Eiler, 2007), (Eiler, et al., 2013).

At natural abundance level, the difference between the abundance of two stable isotopes of one element is very small, therefore relative differences in isotopic ratios can be determined far more

precisely than absolute isotopic ratios. To describe these relative variations, the isotopic abundance is generally reported as  $\delta$  values:

$$\begin{split} \delta_{x} &= \left(\frac{R_{x} - R_{std}}{R_{std}}\right) \cdot 1000 = \left(\frac{R_{x}}{R_{std}} - 1\right) \cdot 1000 \end{split} \tag{5} \text{ (Sharp, 2007)} \\ \text{with} \\ \delta & \text{relative difference in isotopic ratios} \\ R_{x} & \text{ratio of heavy to light isotope in sample} \\ R_{std} & \text{ratio of heavy to light isotope in standard} \\ \text{(-)} \end{split}$$

The  $\delta$  value illustrates the relative difference in isotopic ratios between the sample and a standard material.

The ratio of heavy to light isotope, in this case for oxygen, is defined as:  $R_{\chi} = {}^{18}\text{O}/{}^{16}\text{O}_{x}$ (6).

Variations in the abundance of oxygen isotopes are generally referred to Vienna Standard Mean Ocean Water (VSMOW). Variations in the abundance of carbon isotopes are referred to a carbonate reference material called Vienna Pee Dee Belemnite (VPDB). However, the availability of these international standards is limited, making them expensive. Laboratories therefore commonly use internal standards, which are compared against the international standard.

In this thesis, the initial gas is used as the reference gas. Taking this into account, equation 5 can be rewritten as:

(7)

$$\begin{split} \delta_x &= (\frac{R_x}{R_{inital}} - 1) \cdot 1000 \\ \text{with} \\ R_{initial} & \text{ratio of heavy to light isotope in initial gas} \quad (\text{-}). \end{split}$$

For example, when the abundance of  ${}^{18}O^{16}O$  is studied, equation 7 can be written as:

$$\delta^{18}O = \left(\frac{18_0/16_{0_{\text{sample}}}}{18_0/16_{0_{\text{initial}}}} - 1\right) \cdot 1000 \tag{8}$$

#### 2.3 Variations in the isotopic composition during Knudsen diffusion

Stable isotope fractionation is mainly caused by two processes in nature: equilibrium exchange reactions and kinetic reactions. In this bachelor thesis a kinetic process is investigated, namely diffusion. Diffusion is a process where particles (e.g. ions, molecules) move from a region with a high concentration to a region with a low concentration. There are various diffusion types, but the focus in this bachelor thesis lies on Knudsen diffusion. Knudsen diffusion refers to a diffusive process where the molecules move solely due to molecular flow and it occurs when molecules diffuse through an orifice smaller than the mean free path length. Whereas the mean free path length is the mean distance a molecule can move without colliding with another molecule. The mean free path length is dependent on the pressure, temperature and the diameter of the molecule. The next equation shows the definition of the mean free path length:

$$\lambda = \frac{K_B T}{\sqrt{2} \cdot P \cdot \pi \cdot d^2}$$
(9) (Peter Atkins, 2013)

with

λ	mean free path length	(m)
Ρ	pressure	(Pa)
d	diameter of the molecule	(m).

The diameter for oxygen and carbon dioxide molecules are:

<b>d</b> <sub>oxygen</sub>	358 pm
$d_{carbon\ dioxide}$	407 pm. (J.T.R.Watson, 2005)

To get in the molecular flow regime, the mean free path length of the molecules has to be larger than the orifice the molecules diffuse through. In this thesis the diffusion occur through tiny holes (i.e.  $\mu$ m scale) and at low pressure (see section 3.2). From equation 9 it can be seen that the mean free path length increases as the pressure decreases.

Various processes cause molecules to fractionate. Isotopic fractionation is defined as the enrichment of an isotope relative to another (e.g. initial gas or reference standard). To describe the fractionation a fractionation factor is introduced. The fractionation factor  $\alpha$  is defined as the ratio of any two isotopes in a compound A, divided by the corresponding ratio for another chemical compound B that are compared to each other:

 $\begin{array}{ll} \alpha_{A-B} & = \frac{R_A}{R_B} \\ \text{with} \\ R & \text{abundance ratio of heavier (minor) to lighter (major) isotope} \\ \alpha_{A-B} & \text{isotopic fractionation factor} \end{array} \tag{10} (Sharp, 2007)$ 

The fractionation factor is commonly given in permil:  $10^3 \ln \alpha_{A-B}$ .

For kinetic fractionation, the fractionation factor depends on the difference in velocity of two isotopologues. For molecules of the same gas the kinetic gas theory states:

(Sharp, 2007)

$E_{K1} = I$	$E_{K2} = \frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$		(11)
with			
Eκ	average kinetic energy of the molecules	(L)	
т	mass of the molecules	(kg)	
v	velocity of the molecules	(m/s).	

The fractionation factor is equal to the ratio of the velocities. The ratio of velocities is obtained by rearranging equation 11 (known as Graham's law (Yeung, Young, & Schauble, 2012)):

$$\alpha = \frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$
(12) (Yeung, Young,

& Schauble, 2012)

Based on equation 12, the fractionation factor for each isotopologue can be calculated. For CO<sub>2</sub>, the abundance of the isotopologues  ${}^{16}O^{12}C^{16}O$ ,  ${}^{16}O^{13}C^{16}O$ ,  ${}^{18}O^{12}C^{16}O$  and  ${}^{18}O^{13}C^{16}O$  on mass 44, 45, 46 and 47 will be investigated.

Applying equation 12:

$$10^{3} \ln {}^{47} \alpha_{Knudsen} = 10^{3} \ln \sqrt{\frac{44}{47}} = -32.98\%_{0}$$
$$10^{3} \ln {}^{46} \alpha_{Knudsen} = 10^{3} \ln \sqrt{\frac{44}{46}} = -22.23\%_{0}$$
$$10^{3} \ln {}^{45} \alpha_{Knudsen} = 10^{3} \ln \sqrt{\frac{44}{45}} = -11.24\%_{0}$$

For the  $O_2$ , the isotopologues of interest are  ${}^{16}O{}^{16}O$ ,  ${}^{17}O{}^{16}O$  and  ${}^{18}O{}^{16}O$  on mass 32, 33, and 34.

$$10^{3} \ln^{33} \alpha_{Knudsen} = 10^{3} \ln \sqrt{\frac{32}{33}} = -15.39\%_{0}$$
$$10^{3} \ln^{34} \alpha_{Knudsen} = 10^{3} \ln \sqrt{\frac{32}{34}} = -30.31\%_{0}$$

(13)

For oxygen the  $\alpha$ -values can be related:

 $^{33}\alpha = ^{34}\alpha^{\lambda}$ 

with

 $\lambda$  correlation factor between  $\alpha$ -values (-) (E. D. Young, 2014).

For the diffusion experiments, the fractionation factor  $\alpha$  can be inferred from the isotopic composition of the diffused gas and the residual gas. The so-called Rayleigh equations describe the evolution of the isotopic composition of the diffused and residual gas as a function of the remaining gas fraction. The remaining fraction *f* is defined as:

$f = \frac{X_{residue}}{X_{total}}$			(14)
f	remaining fraction	(-)	
X <sub>residue</sub>	amount of gas in residue	(mL)	
X <sub>total</sub>	total amount of gas	(mL).	

The Rayleigh equation describing the isotopic composition of the residual gas is as follows:

 $\begin{array}{ll} R_{residue} = R_{initial} \cdot f^{a-1} & (15) \mbox{ (Yeung, Young, & Schauble, 2012)} & \\ \mbox{with} & \\ R_{residue} & \mbox{ratio heavier to lighter isotope in residue gas} & (-) & \\ \mbox{} & \mbox{ the fractionation factor} & (-). & \\ \end{array}$ 

A second Rayleigh equation describes the isotopic composition of the diffused sample:

 $R_{diffused} = R_{initial} \cdot \frac{1 - f^{\alpha}}{1 - f}$ (16) (Yeung, Young, & Schauble, 2012)

 $R_{diffused}$  ratio heavy to light isotope in diffused gas (-).

As the results from the mass spectrometer are given in  $\delta$ -values, it is necessary to rewrite equation 14 and equation 15 in a form which contains the  $\delta$  value. This is achieved by substituting equation 7 in equation 15 and in equation 16. For the residue side:

$$\delta_{residue} = (f^{\alpha - 1} - 1) \cdot 1000 \tag{17}$$

and for the diffused side:

$$\delta_{diffused} = (\frac{1 - f^{\alpha}}{1 - f} - 1) \cdot 1000$$
(18).

The complete elaboration to get to equation 17 and equation 18 is displayed in appendix A Rayleigh equations.

From equation 13 a relation between  $\delta^{17}$ O and  $\delta^{18}$ O can be obtained:

$$\Delta^{17}0 = 10^3 \ln\left(\left(\frac{\delta^{17}0}{1000} + 1\right) \cdot 10^3\right) - \lambda \cdot 10^3 \ln\left(\left(\frac{\delta^{18}0}{1000} + 1\right) \cdot 10^3\right)$$
(19)

with

$$\Delta^{17}$$
O variations the triple oxygen isotope abundance (‰).

Equations 23 and 24 apply for each gas, whereas equation 25 is only applicable for oxygen. To illustrate the evolution of isotopic composition Rayleigh plots (i.e. plots of equations 17, 18 and 19) are made.

First for carbon dioxide the Rayleigh plots are illustrated in Figure 3 and Figure 4.



Figure 3. Change in isotopic abundance of  ${}^{16}O^{12}C^{16}O$  and  ${}^{16}O^{13}C^{16}O$  expressed as  $\delta^{13}C$  as a function of the fraction f of the remaining  $CO_2$ .



Figure 4. The change in isotopic composition as a function of the fraction f of CO<sub>2</sub> mass 46.

For oxygen the Rayleigh plots are shown in Figure 5, 6 and 7.



Figure 5. The evolution of the isotopic composition as a function of the fraction f of O<sub>2</sub> mass 33.



Figure 6. The evolution of the isotopic composition as a function of the fraction f of O<sub>2</sub> mass 34.



Figure 7. The evolution of the triple  $O_2$  isotope  $\Delta$  <sup>17</sup>O as a function of the fraction *f*.

### 3 Working method

#### 3.1 Experimental set-up

To study Knudsen diffusion, a set-up has to be designed where a gas diffuses in the molecular flow region (i.e. low pressure and small holes) so that the mean free path length is larger than the diameter of the holes. A large part of this set-up was already designed for a previous project. However, a critical part of it was limiting the capabilities of this set-up. This critical part is where the diffusion takes place.

The set-up is mostly made of glass and a few stainless steel parts, mostly connecting parts. A schematic of the set-up is shown in Figure 8.



Figure 8. Schematic of the diffusion set-up, A denotes the valve to the vacuum pumps, B denotes where the gas is injected, C shows the flow restriction where the diffusion takes place, D and E are positions a vial could be mounted to trap the diffused gas. HV and FV denotes the high vacuum pump and fore vacuum pump respectively. The reservoir has a size of 5L.

The experimental set-up can basically be split into two parts, the left hand side of the flow restriction and the right-hand side of the flow restriction. The left-hand side of the flow restriction is used for injecting the gas (although the residual gas can also be trapped at this side), and the right-hand side is used to trap the diffused gas.

As shown, there are nine valves in the set-up. These valves are meant for high vacuum, which means that when they are closed, no air is allowed into the set-up (ideally). These valves are used to connect the fore- and high-vacuum pump to the set-up, as well as for vials used for trapping the gas. On the right-hand side three vials can be used to trap the diffused gas. The three valves make it possible to investigate the time dependency.

The large reservoir (5 L) is used to obtain a low pressure (high mean free path length) and to still have enough gas available for a (clumped) isotope measurement (about 0.5 mL ASTP gas is required for a clumped isotope measurement and about 0.05mL ASTP for a conventional stable isotope measurement). However, a drawback of this big reservoir is that it is very time-consuming to evacuate it. To ensure this time frame is as short as possible, a few changes in the experimental set-up were made. The area of the tubing connecting the vacuum pumps to the glass line has been

doubled. This leads to an increase in the vacuum and decreased the time needed for evacuating the big reservoir.

An important piece of this set-up is the diffusion part denoted by C in the schematic of the set-up. Previous measurements were carried out with diffusion through capillaries (Figure 9). However, for this study the capillaries are replaced by perforated aluminium foil. The aluminium foil is perforated with a laser (Compex 102, Eximer-laser 193 nm).

The width of this laser beam determines the diameter of a hole in the foil. This makes it possible to create tiny holes (i.e.  $\mu$ m scale). As mentioned in theory, it is necessary that the holes are smaller than the mean free path length.



Figure 9. Glass capillaries acting as flow restriction. 19 capillaries are placed in a septum(diameter 5 mm), leaving the outer area free to place and remove the septum without harming the capillaries.

Figure 9 shows how the capillaries are positioned within a septum. Inserting the capillaries had to be done manually. Therefore the amount of capillaries used cannot be large. As shown in Figure 9, the capillaries can only be inserted in a small area of the septum, as the outer area has to be free to place (or remove) the septum without harming the capillaries. These capillaries tend to break easily as they are made of glass. The capillaries were replaced by different aluminium foils, which contain up to several hundred holes.

To perform stable isotope measurements, the diffusion part of the set-up is crucial. The diffusion used to take place in capillaries, but as already mentioned they have been replaced by an aluminium foil. This is a part of improving the set-up. The aluminium foil has the advantage that there is no length (except for the thickness of the foil) and are made with a laser. This makes it possible to get a large amount of holes in a small area. An example of such a foil is displayed in Figure 10.



Figure 10. Perforated aluminium foil acting as flow restriction (diameter of the foil is 10 mm). There appears to be a large square in this aluminium foil, but there are actually 625 holes with a 23 µm diameter within this square (left with light source to show the holes, right without light source ).

Figure 10 shows that the small holes cannot be seen without a light source behind it. This illustrates their size. In this foil the amount of holes is 625, it should be noted that this would increase the diffusion speed significantly compared to 24 capillaries. The holes of the foil are 23  $\mu$ m, which makes it possible to agree to the molecular flow regime. But in order to get to the molecular flow regime the pressure has to be low enough. To achieve this, a fore- and high-vacuum pump are used. To get this vacuum, the set-up has to be leak-tight. This means that every metal connection has to be tightened properly.

The 625 holes aluminium foil has a thickness of 12  $\mu$ m (i.e. equal to regular aluminium foil). When such a thin foil is placed within the set-up and tightened in a metal connection it tends to break easily. Using them was risky as a tiny defect in the foil could lead to false measurements.

Therefore, a 30  $\mu$ m foil is used. The thicker aluminium foil does not break as fast as the thin aluminium foil and therefore the diffusion part is more likely to be leak-tight. The perforated foil with 12um diameter holes was provided by Andreas Pack from the University of Göttingen, Germany. For the 30  $\mu$ m hole foil, the foil had to perforated. As mentioned, this was possible with the help of a laser. At first, to be able to compare the foil with the capillaries, 19 holes were perforated. The laser was controlled manually, therefore an amount of 625 holes would consume a lot of time. Besides time-consuming, getting such a large amount of holes in such a small area is hard to manage.

#### 3.2 Stable isotope measurements

A measuring protocol has been made referring to Figure 8. Before measurements are started at valve C (residue side) and valve F,G,H (diffused side) a glass vial should be attached (and evacuated). These vials have to contain molecular sieve for oxygen measurements. This is because oxygen cannot be frozen in with liquid nitrogen. Therefore an adsorbing material is necessary. These vials are used to trap diffused and residual gas.

The experimental measurements are as follows:

- Evacuate the system (to  $2 \cdot 10^{-5}$  mbar)
- Close valve (C) to the big reservoir (prevent any gas to go to reservoir)
- Introduce needle to set-up (valve B)
- Open valve (C) to the big reservoir again (the pressure should remain constant now)
- Close valve A to the vacuum pump
- Inject the x amount of either oxygen or carbon dioxide
- place a vial at D, F,G or I (in a Dewar flask filled with liquid nitrogen)
- Wait until the desired amount of diffused gas is reached and close valve E
- Introduce gas in mass spectrometer.

The principle of a gas-source isotope ratio mass spectrometer is shown in Figure 11. The main components of the GS-IRMS are:

- One bellow for the reference (initial) gas and one for the sample gas (diffused or residue)
- Switching block to switch between the sample and reference gas
- An ion source which ionizes the molecules by electron bombardment
- A magnet which deflects the ionized molecules (depending on m/q ratio)
- Faraday cups as ion collectors.

Two mass spectrometers are used, for conventional stable isotope measurements the Finnigan  $\Delta$  plus XL was used, and for clumped isotope measurements on CO<sub>2</sub> the Finnigan MAT-253 was used that can register the six ion currents 44 to 49 simultaneously.



Figure 11. GS-IRMS with two bellows (reference and sample side) an ion source to ionise the isotopes, a magnet which deflects the path of the ionized molecules and an ion collector collecting the ions (Sharp, 2007).

#### 3.3 Calibration gas volume in mass spectrometer

As the pressure meter mounted to the big reservoir was not very accurate, another method to determine the amount of diffused gas is established. This method involves the IRMS. The mass spectrometer contains two bellows, which can be filled with gas. For measurements, one bellow was filled with the initial gas and the other bellow was filled with the sample.

When a gas is inserted in the IRMS, the IRMS will give a certain intensity. By injecting several amounts of gas (from 0.5 to 3 mL), a calibration line was determined. This method is applied for calibrating the IRMS for  $CO_2$  and  $O_2$ .



Figure 12. Intensity as a function of the amount of carbon dioxide

The formula for the regression line is:

y = 1531.5x + with	+ 178.47	
y x	intensity on the mass spectrometer amount of carbon dioxide inserted	(mV) (mL).

From the least squares method the error in the slope has been determined which is:  $\pm 0.115$ . This leads to an error in the fraction of gas *f* of: 0.11.

Furthermore, the calibration for oxygen has been established, as shown in the figure on the next page.



Figure 13. Intensity as a function of the amount of oxygen.

The formula for the regression line for oxygen is:y = 1040.9x - 29.667withyintensity on mass spectrometerxamount of oxygen inserted(mL).

For both calibration curves there is an error in the slope. This error is proportional to the error in the fraction f of the gas. The error is calculated with the least squares method, which was part of the statistical method employed in Excel. This lead to an error of 0.027 in the regression line y. which results in an error of 0.03 in the fraction f.

As the number of measurements is low (3 < n < 6), the student t-distribution has been used to get reliable errors. The notation of the Student's t-distribution is as follow: SE·t0.95. This means that the standard deviation is multiplied with the corresponding t-value for a 95% confidence limit. See appendix C.

### 4 Experimental results

### 4.1 Diffusion experiments with O<sub>2</sub>

At first, measurements were carried out with oxygen to investigate the diffusional flow rate and the change in isotopic composition ( $\delta^{18}$ O,  $\delta^{17}$ O and  $\Delta^{17}$ O values). For the first measurements, the set-up was not ideal (i.e. there was a leak in the set-up). After the leak had been found and fixed, a new set of diffusion experiments was carried out with oxygen.

Figure 14 illustrates the amount of holes/capillaries and the corresponding flow rate at a certain mean free path length (for the leaking set-up).



Figure 14. Diffusional flow rate vs. the mean free path length obtained with the leaking set-up.

Also for the leak-tight set-up, the flow rate is illustrated vs. the mean free path length. This is shown in Figure 15 on the next page.



Figure 15. Diffusional flow rate vs. The mean free path length obtained with the leak-tight set-up.

#### 4.2 Isotopic composition of oxygen

#### 4.2.1 Leaking set-up

The principle of the measurements was that the isotopic composition of the residual gas was heavier than the initial gas, whereas the isotopic composition of the diffused gas was lighter than the initial gas. The enrichment of  $\delta^{18}$ O and  $\delta^{17}$ O varied with the amount of gas that diffused. For small amounts of diffused gas, the isotopic composition was light relative to the initial gas. When larger amounts of gas diffused the isotopic composition got heavier and heavier.

The enrichment of the  $\delta^{18}$ O and  $\delta^{17}$ O were in the range of 5-20 ‰ and 2-10 ‰ respectively for the residue gas. This means that the isotopic composition is 5-20 ‰ and 2-10 ‰ heavier than the initial gas. For the diffused gas the enrichment of the  $\delta^{18}$ O and  $\delta^{17}$ O were in the range of -10 to -20 ‰ and -5 to -10 ‰ respectively for the diffused gas. As mentioned in section 2.3, the <sup>33</sup> $\alpha$  and <sup>34</sup> $\alpha$  are correlated with a  $\lambda$ -value(which differs from 0.5 for kinetic to 0.53 for equilibration processes). To illustrate these small differences in the triple oxygen isotope, a third plot was carried out: the  $\Delta^{17}$ O plot.

First the residual results with oxygen are shown, followed by the results on the diffused side. The diffusion experiment was carried out with capillaries (i.e. 19 with diameter of 23  $\mu$ m) and 2 aluminium foils (i.e. 100 holes and 19 holes with a diameter of 30  $\mu$ m). With the 19 holes foil and 19 capillaries only the residual gas has been analyzed.



Figure 16. The enrichment in the  $\delta^{18}$ O and  $\delta^{17}$ O in the residual gas are shown (for diffusion experiments done with 2 aluminium foils and 1 septum with capillaries). The y-errors are smaller than the symbols and therefore not shown. Also, the variations in triple isotope are shown.



Figure 17. The enrichment of  $\delta^{18}$ O and  $\delta^{17}$ O of the diffused gas is illustrated along with the variations in the triple oxygen isotope.

From the results in  $\delta^{18}$ O and  $\delta^{17}$ O (Figure 16 and Figure 17) the  $^{34}\alpha$  and  $^{33}\alpha$  values can be determined. From these  $\alpha$ -values, the  $\lambda$ -value can be calculated. These results are illustrated in Table 3:

	1000 ln( <sup>33</sup> α) (‰)	1000 ln ( <sup>34</sup> α) (‰)	$\lambda$ -value (-) [= 1000ln <sup>33</sup> $\alpha$ /1000ln <sup>34</sup> $\alpha$ ]
Residue(100 holes)	11.90 ±1.6	-22.9 ±3.3	0.5226±0.015
Diffused(100 holes)	-11.75 ±0.6	23.1 ±1.1	0.5093±0.06
Residue(19 holes)	14.91 ±1.6	-28.1±1.9	0.5298 ± 0.007
Residue(19 capillaries)	-16.5 ±1.3	-31.4 ±2.6	0.5107± 0.033

Table 3. The  $^{33}\alpha$  ,  $^{34}\alpha$  and  $\lambda$  values calculated for the residual and diffused gas.

To check whether the diffusion experiment was in the molecular flow regime, a plot was established which shows the correlation between mean free path length and the fractionation factor. This plot is shown in Figure 18.



Figure 18. Mean free path length vs. the 1000 ln  $^{33}\alpha$   $^{34}\alpha$  values.

After fixing the leak and minor adjustments to the set-up another set of diffusion experiments was carried out.

#### 4.2.2 Leak-tight set-up





Figure 19. The enrichment in the  $\delta^{18}$ O and  $\delta^{17}$ O in the residual gas are shown. The y-errors are smaller than the symbols and therefore not shown. Also, the variations in the triple oxygen isotope are shown.



Figure 20. The enrichment in the  $\delta^{18}$ O and  $\delta^{17}$ O in the diffused gas are shown. The y-errors are smaller than the symbols and therefore not shown. Also, the variations in the triple oxygen isotope are shown.

From the leak tight set-up also a graph with the fractionation factors vs. the mean free path length was established and illustrated in the next figure.



Figure 21. The 1000 ln  $^{33}\alpha$  and  $^{34}\alpha$  values(from the diffused samples) vs. mean free path length.

### **5** Discussion

#### 5.1 Flow rate of oxygen

The experiments done with oxygen resulted in a diffusional flow rate and a change in isotopic composition of the gas. For the diffusional flow rate only the results obtained with the leak-tight setup will be shown and compared with the predicted values, calculated with the equations from section 2.1.

For three different amounts of gas, the flow rate was observed (see Table 4). The observed values deviate with a factor 10 from the expected flow rates. A cause might be the size of the orifice. When applying an error of  $\pm 1.5 \,\mu$ m (i.e. the precision of the laser) in the radius of the orifice, the slope (see Figure 22) is affected significantly. Figure 22 illustrates the pressure drop (i.e. the diffusion speed) as a function of time.

Initial pressure	Expected molecular flow	Measured molecular flow
(mbar)	rate (100 holes)(mL/h)	rate (100 holes)(mL/h)
0.3	8.3	0.75 ± 0.37(SE·t <sub>0.95</sub> )
0.2	5.5	0.5769 ± 0.23(SE·t <sub>0.95</sub> )
0.1	2.8	0.225 ±0.02 (SE·t <sub>0.95</sub> )

Table 4.	Molecular	flow rates	s on the	e leak tight	set-up	expected	and measure	ed compared

From each plot it can be seen that the final observed pressure is larger than expected. This means that the observed flow rate is lower than expected.

For the error in the radius of the holes, 1.5  $\mu$ m has been chosen (which is the precision of the laser of 10%). From the plots it can be concluded that the size of the orifice has a significant effect on the molecular flow rate. This would suggest that the holes in the aluminium foil are smaller than expected. Investigating the holes in the foil should verify whether this is indeed the case. The next table shows the flow rates expected according to the molecular flow equations.



Figure 22. The logarithmic pressure drop as a function of time. The first plot (blue) illustrates the pressure drop for 1.5 mL  $O_2$ . The second plot (green) shows the pressure drop for 1 mL  $O_2$  and the last plot (red) shows the pressure drop for 0.5 mL  $O_2$ . The error in the expected value is determined with the precision of the used laser (10%) which corresponds to  $\pm$  1.5  $\mu$ m.

To visualize the observed pressure drop, the pressure drop should be monitored continuously. For these plots, only the starting pressure and final pressure can be determined, this is due to the pressure sensor used for this thesis did not show the actual pressure. Furthermore, the pressure range of this sensor is from 0.01 mbar to 1 mbar. Because of the mentioned shortcomings of the pressure sensor, this pressure sensor cannot be used to determine the fraction of gas which is left. Therefore, real-time pressure monitoring is not possible. Replacing the pressure sensor by one which can determine the pressure sensor more precise (i.e. one that has a pressure range of 0.001 to 0.5 mbar) would solve this problem.

#### 5.2 Isotopic composition of oxygen

To compare the change in isotopic composition of the gas to theory, the experimental results are plotted in the Rayleigh-plots from section 2.3 (see Fig. 3, 4 and 5). The preliminary results presented here were obtained with a leaking set-up. As the leak was on the right hand side of the set-up (i.e. the diffused side) it might not have affected the experimental results on the left hand side (i.e. the residue side). However it is possible that the leak affected the magnitude of a possible back diffusion flux.

#### 5.2.1 Leaking set-up experiments



Figure 23. The measured change in isotopic abundance of  $\delta^{18}$ O and  $\delta^{17}$ O vs. the expected change in isotopic abundance on the residue side. And the variations in triple oxygen isotope abundance (<sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O) denoted as  $\Delta^{17}$ O vs. a 0.53 reference line. It should be noted that the y-errors for  $\delta^{18}$ O and  $\delta^{17}$ O are not illustrated as they are smaller than the symbols.

From Figure 23 it can be seen that the experimental results generally agree within error with the expected values (blue). It can also be seen that the values obtained for  $\delta^{18}$ O and  $\delta^{17}$ O show a similar pattern but differ approximately by a factor of 0.5. This is due to the fact that  $\delta^{17}$ O and  $\delta^{18}$ O are correlated (in a mass-dependent manner) with a  $\lambda$ -value of 0.5 (for kinetic processes) to a  $\lambda$ -value of 0.53 (for equilibrium processes) (Young, 2002). To illustrate these small variations in  $\delta^{17}$ O, caused by these variations in the  $\lambda$  –value, the abundance of <sup>17</sup>O is given as  $\Delta^{17}$ O relative to a reference line (E. D. Young, 2014), Young, 2002).

It should be noted that the enrichment in isotopic abundance can be lower than the predicted value. This is caused by the fact that the prediction is based on a molecular flow. However, due to viscous flows it is possible that the fractionation is less than predicted. Because the flow rate and the determined fractionation factor vary with the mean free path length, at least the experiments at the low mean free path length were not yet in the molecular flow regime.

The result at f = 0.5 (with 100 holes foil) appears to be an outlier which does not correspond to theory. From the plot it appears that this result deviates by 10‰ from the expected  $\delta^{18}$ O value and 5‰ for the  $\delta^{17}$ O value. This can be caused by several factors. Possibly, the *f* value is not calculated properly or the amount of gas injected was too large, so that the diffusion did not occur within the molecular flow regime. Another cause can be back diffusion from O<sub>2</sub> (from diffused to residue). In general, back diffusion can affect the apparent fractionation factor.

The results from the diffusion experiments can be found in Table 5. By comparing them to predicted fractionation factors it can be concluded that the results correspond within a 3  $\sigma$  error with the predicted values. The results obtained with the capillaries and 19 holes aluminium foil are not sufficient as for both only 3 experiments were carried out. The data for these two flow restrictions however, seem to correspond to theory within a 1  $\sigma$  error.

It appears that the results obtained by Yeung et al. (2012) (see Table 5) and the results from this thesis also corresponds within error.

Now the results on the diffused side will be discussed. As the diffusion process is a slow process, the diffusion experiment was carried out, only with the 100 holes foil.



Figure 24. The measured change in isotopic abundance of  $\delta^{18}$ O and  $\delta^{17}$ O vs. the expected change in isotopic abundance on the diffused side. And variations the triple oxygen isotope abundance (<sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O) denoted as  $\Delta^{17}$ O vs. a 0.53 reference line.

From the plot of the results on the diffused side, it can be seen that the results do not correspond to theory within error. The observed values are approximately 4 ‰ to 7‰ heavier than the theoretical

prediction. The fact that these measurements are systematically off, indicates that there is a defect in the set-up. It was already known there was a leak, which will most likely be the cause of the systematic offset. The fractionation factors were calculated as 1000 ln ( $^{34}\alpha$ )= -(23.1 ±3.1(SE·t<sub>0.95</sub>) ‰ and 1000 ln ( $^{33}\alpha$ )= -11.75 ±1.7(SE·t<sub>0.95</sub>) ‰ on the basis of the diffused O<sub>2</sub>.

Yeung et al. (2012) obtained the following fractionation factors on the diffused side: 1000 ln ( $^{34}\alpha$ )= -22.15‰ and 1000 ln ( $^{33}\alpha$ )= -11.28 ‰.

The diffused results correspond to the results obtained by Yeung et al. (2012). For these results Yeung et al (2012) mentioned back diffusion as the most important factor for the deviation of the diffused results from the theoretically predicted value.

The effect of back diffusion is calculated with equation 20. Back diffusion is described with the following equation (Yeung, Young, & Schauble, 2012):

$$\alpha_{bd} = (a_i - 1) \left( 1 - \frac{P_{ds}}{P_{us}} \right) + 1$$
(20)

with

$\alpha_{bd}$	back diffusion fractionation factor	(-)
a <sub>i</sub>	fractionation factor of sample <i>i</i>	(-)
$P_{ds}/P_{us}$	ratio of downstream pressure and upstream pressure	(-).

The fractionation factors calculated are again written in 1000 ln  $\alpha$  notation. For <sup>34</sup> $\alpha$  the 1000 ln  $\alpha_{bd}$ = (-2.7 ± 0.43)‰ for <sup>33</sup> $\alpha$  the 1000 ln  $\alpha_{bd}$ = (-5.3 ± 0.9)‰. From these results it can be concluded that the back diffusion flux (caused by the leak), affects the measurements significantly.

Laurence Yeung suggested that the inner surface of the pressure sensor (on the diffused side) could possibly interact with the diffused gas. Such a surface effect might alter the isotopic composition of the gas. He also suggested to replace the molecular sieve with silica gel, because he observed that the interaction with mole sieve can partially reset the clumped isotopic composition of  $O_2$  (personal communication, April 19, 2016).

The effect of molecular sieve on the  $\delta^{18}$ O and  $\delta^{17}$ O fractionation of the gas was investigated by measuring the initial gas vs. the same gas but frozen back on the mole sieve and then released back to the mass spectrometer. This way it was investigated whether the effect of molecular sieve could be neglected or not. The interaction with the mole sieve changed the  $\delta^{18}$ O value by (-0.22 ±0.006)‰ and the  $\delta^{17}$ O value by (-0.07 ±0.02)‰. The influence of molecular sieve on the isotopic composition of O<sub>2</sub> was also investigated by O. Abe (2008). He observed a shift in  $\delta^{18}$ O of (0.101 ±0.003)‰ and in  $\delta^{17}$ O of (0.051 ±0.021)‰ (Abu, 2008). From comparing these values it can be concluded that Abe (2008) observed a smaller effect of the mole sieve on the isotopic composition. A likely cause is that the molecular sieve was not sufficiently heated (for the experiment conducted for this thesis). Even though there are minor effects on the fractionation due to the molecular sieve, it does not explain the large deviation that was observed.

An overview is shown for the results obtained with 100-holes aluminium foil, the results obtained by Yeung et al. (2012) and the theoretically predicted value.

	1000 ln ( <sup>33</sup> α) (‰)	1000 ln ( <sup>34</sup> α) (‰)	$\lambda$ -value (-) [= ln <sup>33</sup> α /ln <sup>34</sup> α]
Residue (100)	-14.47 ±1.4(SE·t <sub>0.95</sub> )	-28.1 ±3.3(SE·t <sub>0.95</sub> )	0.5105±0.005(SE·t <sub>0.95</sub> )
Diffused (100)	-11.75 ±1.7(SE·t <sub>0.95</sub> )	-(23.1 ±3.1(SE·t <sub>0.95</sub> )	0.5093±0.006(SE·t <sub>0.95</sub> )
Residue (19foil)	-14.91 ±1.6	-28.13 ±1.9	$0.5298 \pm 0.02(SE \cdot t_{0.95})$
Residue(19 capillaries)	-16.5 ±1.3	-31.4± 2.6	0.5107± 0.0033
Residue (Yeung)	-15.41	-30.39	0.5071
Diffused (Yeung)	-11.28	-22.15	0.5092
Theoretical prediction	-15.39	-30.31	0.5076

Table 5. The  $^{33}\alpha$ ,  $^{34}\alpha$  and  $\lambda$  values calculated for the residue and diffused gas compared to the expected values.

From Figure 18 it can be seen that there is a large spread in the  $\alpha$  values. It is possibly related to the leak, although these results are derived from the residue measurements. It is important to know whether the process is in the molecular flow regime. If that was the case, the results could be used for calibrating a new mass spectrometer. If the diffusion does not take place in the molecular flow regime, the results cannot be used for calibrating the new mass spectrometer.

Therefore, it is important to carry out measurements with smaller amounts of gas (e.g. 0.1-1mL) to see if the measurements are actually in the molecular flow regime. To increase the accuracy of the measurements, the molecular sieve has to be replaced by silica gel and the pressure sensor on the diffused side should be removed from the glass line. Measurements after these adjustments should show whether the set-up was indeed improved.

#### 5.2.2 Leak-tight set-up

These diffusion experiments were carried out with the 100 holes foil only. With this foil, more data could be obtained than with a 19 holes foil or the 19 capillaries.



Figure 25. The measured change in isotopic abundance of  $\delta^{18}$ O and  $\delta^{17}$ O vs. the expected change in isotopic abundance on the residue side. And variations in the triple oxygen isotope abundance (<sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O) denoted as  $\Delta^{17}$ O vs. a 0.53 reference line.

The results from Figure 25 were obtained in a leak tight set-up. It can be seen that the results are systematically off. On average the  $\delta^{18}$ O and  $\delta^{17}$ O the results are 4-8 ‰ lighter than the predicted value. At *f*= 0.42 there is possibly an outlier which will not be taken into account for the calculations of the fractionation factors.



Figure 26. The measured change in isotopic abundance of  $\delta^{18}$ O and  $\delta^{17}$ O vs. the expected change in isotopic abundance on the diffused side. And variations in the triple oxygen isotope abundance (<sup>16</sup>O, <sup>17</sup>O, <sup>18</sup>O) denoted as  $\Delta^{17}$ O vs. a 0.53 reference line.

Figure 26 illustrates the results on the diffused side. It can be seen that the results correspond better to the predicted value than with the leaking set-up. There are still experiments where the results are deviating from the predicted value with 3‰.

It appears that the fractionation for the residual samples agree within a 3  $\sigma$  error to the predicted values. Compared to the fractionation factors obtained in the leaking set-up on the residual side, the results got worse. A concrete cause has not been found however, it might be that not all the oxygen was trapped, and therefore some loss of oxygen occurred.

The diffused agree to theory within a 1  $\sigma$  error (see Table 6). Compared to the values obtained with the leaking set-up, the results improved.

As the results on the diffused side are corresponding to the predicted value, the results on the residual side should agree to theory as well. However the residual samples are lighter than expected, which suggests that there is some oxygen lost while taking the sample. Further research should verify this.

For investigating the effects of the mean free path length, diffusion experiments were carried out with 0.5 mL gas (i.e. a mean free path length of 726  $\mu$ m). From the results (see Table 6) the fractionation factors appear to be larger than the theoretical prediction, which is not possible. It might be caused by the fact that the *f*-value cannot be determined precise. For these measurements at high mean free path length (relative to 242 and 363  $\mu$ m) both the diffused side and residual side correspond to the predicted values within 1  $\sigma$  error. For these diffusion experiments it seems that there is no oxygen loss, which might suggest that lower amounts of gas are easier to freeze in.

	1000 ln ( <sup>33</sup> α)	1000 ln ( <sup>34</sup> α)	λ-value (-)
	(‰)	(‰)	$[= \ln^{33} \alpha / \ln^{34} \alpha]$
Residue (100)	-12.94	(-25.4	0.5089 ±0.003(SE·t <sub>0.95</sub> )
	±1.1(SE·t <sub>0.95</sub> )	±1.8(SE·t <sub>0.95</sub> )	
Diffused (100)	-14.2	-28.1	0.5052 ± 0.0015(SE·t <sub>0.95</sub> )
	±2.2(SE·t <sub>0.95</sub> )	±1.3(SE·t <sub>0.95</sub> )	
Residue(100) 726 μm	-31.7 ±1.7	-15.8 ±0.6	0.50± 0.01(SE·t <sub>0.95</sub> )
	(SE·t <sub>0.95</sub> )	(SE·t <sub>0.95</sub> )	
Diffused 100) 726 µm	-29.3	-15.7	0.533±0.05(SE·t <sub>0.95</sub> )
	±2.6(SE·t <sub>0.95</sub> )	±0.7(SE·t <sub>0.95</sub> )	
Theoretical prediction	-15.39	-30.31	0.5076

Table 6. The 1000 ln  $^{33}\alpha$  , 1000 ln  $^{34}\alpha$ , and  $\lambda$  values calculated for the residue and diffused gas compared to the expected values.

The fractionation factors are calculated from the diffused gas samples. The results on the residual (at mean free path lengths of 242 and 363  $\mu$ m) side are systematically off and therefore not useable for the fractionation vs. mean free path length plots. The cause of the offset might be that not all the oxygen is frozen in.



Figure 27. The fractionation factors  ${}^{34}\alpha$  and  ${}^{33}\alpha$  (from diffused samples) vs. the mean free path.

Figure 27 illustrates the fractionation factors vs. the mean free path length obtained from the diffused samples. From the results it can be seen that at mean free path lengths of 242 and 363  $\mu$ m there is a spread which indicates the reproducibility is not reliable. More data should be obtained to confirm this statement. At a mean free path length of 726  $\mu$ m, the illustrated data points correspond to the predicted value. More data should be acquired to illustrate the reproducibility. Although there is insufficient data, the data suggests that the mean free path length affects the measurements. More data should be acquired to confirm this suggestion.

To improve the diffused samples even more, it is possible to mount the pressure sensor indirectly to the set-up. This would prevent the diffused gas to interact with the pressure sensor. Another method of improving the diffusion experiment is terminating fractionation caused by back-diffusion. With a 100 holes foil, the process of freezing in gas is not as fast as the diffusion process. This possibly increased the back diffusion flux. By using a foil which contains less holes, the back diffusion can possibly be neglected. An alternative is using more vials(in liquid nitrogen) to decrease the duration of adsorbing process.

### 6 Conclusion

To study Knudsen diffusion an already existing set-up was used. This set-up was not yet functioning optimally. The diffusion experiments were very time consuming due to a limited amount of orifices (for the diffusion). The set-up has been improved with multiple adjustments. The flow restriction was replaced. Originally a septum with manually inserted capillaries (with a diameter of 23  $\mu$ m) was used. Because this had to be done manually the maximum amount of capillaries that could be inserted was on the order of 25. The septum was replaced by a perforated aluminium foil. The perforation of this aluminium foil was done with a laser. By doing this with a laser a lot of holes could be created (i.e. up to hundreds of holes) with a diameter of 30  $\mu$ m. The diffusion time with up to 25 capillaries was in the magnitude of 10-40 hours and has been decreased to 1.5 hour by the use of the aluminium foil with hundreds of holes.

Also evacuating the set-up was time consuming (1-2 hours). To get this done faster the glass tubes in the set-up were increased from 0.25 to 0.5 inch. With this adjustment the evacuation time decreased to 20 minutes.

Initially, the diffusion experiment were performed with a leaking set-up. Diffusion through an aluminium foil which contained 100 holes with a diameter of 30 µm resulted in fractionation factors of: 1000 ln ( $^{34}\alpha$ ) =(-28.1 ±3.3(SE·t<sub>0.95</sub>))‰ and 1000 ln( $^{33}\alpha$ ) =(-14.47 ±1.4(SE·t<sub>0.95</sub>)) ‰ for the residual gas and (-11.75 ±0.6)‰ and (-23.1 ±1.1) ‰ for the diffused gas. The results on the residue side appear to agree within 1 $\sigma$  error to the predicted values (-15.39‰ and -30.31‰). The results on the diffused side do not correspond to the predicted values. Possible reasons for deviation between measured results and predicted values are: (i) Not in the molecular flow regime (i.e. mean free path length smaller than size of orifice), (ii) back diffusion occurs or (iii) fractionation was caused by the pressure sensor/molecular sieve.

After fixing the leak, again diffusion experiments were carried out. At a mean free path length of 726  $\mu$ m this resulted in a molecular flow rate of 0.225±0.08 (SE·t<sub>0.95</sub>) mL/h. Compared to the expected 2.7 mL p/h, the observed value is about 10 times lower than the expected flow rate. This might be caused by smaller holes in the flow restriction than expected. The same applies for the observed flow rates at mean free path lengths of 242 and 363  $\mu$ m, where the expected molecular flow rates were 8.3 and 5.5 mL/h respectively.

For the residual gas the fractionation factors were: 1000 ln ( $^{34}\alpha$ ) = (-25.4 ±1.8(SE·t<sub>0.95</sub>))‰ and 1000 ln ( $^{33}\alpha$ )= (-12.94 ±1.1(SE·t<sub>0.95</sub>)) ‰. With the diffused samples the following fractionation factors were obtained: 1000 ln ( $^{34}\alpha$ ) = (-28.1 ±1.3(SE·t<sub>0.95</sub>))‰ and 1000 ln ( $^{33}\alpha$ )= (-14.2 ±2.2(SE·t<sub>0.95</sub>)) ‰. The corresponding  $\lambda$  value is: 0.5052 ± 0.0015(SE·t<sub>0.95</sub>).

When increasing the mean free path length from to 726 µm the following fractionation factors were obtained: 1000 ln ( $^{34}\alpha$ ) = (-31.7 ±1.7 (SE·t<sub>0.95</sub>))‰ and 1000 ln ( $^{33}\alpha$ )= (-15.8 ±0.6 (SE·t<sub>0.95</sub>)) ‰. The  $\lambda$  value, derived from these results is 0.50±0.01(SE·t<sub>0.95</sub>). On the diffused side the fractionation factors obtained were: 1000 ln ( $^{34}\alpha$ ) = (-29.3 ±2.6(SE·t<sub>0.95</sub>))‰ and 1000 ln ( $^{33}\alpha$ )= (-15.7 ±0.7(SE·t<sub>0.95</sub>)) ‰. The corresponding  $\lambda$  value is: 0.533 ± 0.05(SE·t<sub>0.95</sub>).

By fixing the leak, the diffused samples correspond to theory within a  $1\sigma$  error. However, the observed deviations can still be caused by not being in the molecular flow regime or not freezing in all the oxygen.

The data suggests that the mean free path length affected the measurements. Increasing the mean free path length resulted in fractionation factors closer to the predicted value. The reason is that the diffusion approaches a pure molecular flow regime at lower starting pressures (higher mean free path lengths).

Increasing the quality of the diffused samples (for clumped isotope measurements) might be established by detaching the pressure sensor from the diffused side. As the gas could fractionate because of interaction with the metal surface of the pressure sensor. Also a smaller amount of holes can be used to neglect the back diffusion flux. An alternative to increase the freezing process is using multiple vials for freezing in the sample gas.

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### References

- Abu, O. (2008). Isoptope fractionation of molecular oxygen during adsorption/desorption by molecular sieve zeolite. *Rapid communications in Mass spectrometry*, 2510-2514.
- E. D. Young, L. Y. (2014). On the Δ 170 budget of atmospheric O2l. *Journal of Geophysical reserach*, Edward D. Young<sup>↑</sup>, Laurence Y. Yeung, Issaku E. Koh.
- Eiler, J. M., Clog, M., Magyag, P., Piasecki, A., Stolpher, D., Deerberg, M., . . . Schwieters, J. (2013). A high resolution gas-source isotope ratio mass spectrometer. *Int. J. Mass spectrom*, 45-46.
- *Ideal Vacuum products.* (2016, Mei 25). Retrieved from Ideal Vacuum products: http://idealvac.com/
- Indirect-gas-dependent pressure measurement. (2016, 5 25). Retrieved from Pfeiffer Vacuum: https://www.pfeiffer-vacuum.com/en/know-how/vacuum-measuring-equipment/fundamentals-of-total-pressure-measurement/direct-gas-independent-pressure-measurement/
- J.T.R.Watson. (2005). *NPL.* Retrieved 03 01, 2016, from Kaye & Laby Tables of Physical & Chemical Constant: http://www.kayelaby.npl.co.uk/general\_physics/2\_2/2\_2\_4.html
- Knudsen, M. (1933). The kinetic theory of gases. London: London Methuen & CO. LTD.
- Linde, M. v. (2015). Isotopic fractionation of CO2 due to Knudsen diffusion. Utrecht.
- *Low-Pressure Effusion Of Gases.* (2005). Retrieved from hope.edu: http://www.chem.hope.edu/~polik/Chem345-2005/gaseffusion.htm
- M., E. J. (2007). "Clumped-isotope" geochemistry. Earth planet Sci. Lett 262, 309-327.
- Peter Atkins, J. D. (2013). *Elements of Physical Chemistry*. Oxford: Oxford University Press.
- Shafer, D. S., & Zhang, Z. (2012). *Introductory Statistics*. North Carolina, United states of America.
- Sharp. (2007). Principle of Stable Isotope Geochemistry. Michigan: Prentince hall.
- Yeung, L. Y., Young, E. D., & Schauble, E. A. (2012, 9 26). Measurements of 180180 and 170180 in the atmosphere and the role of isotope-exchange reaction. *Journal of Geophysical Research*, pp. 1-20.

### A Original project description

Het project dat plaatsvindt aan de universiteit in Utrecht zal bestaan uit literatuurstudie en experimenteren.

De opdracht is het experimenteel bepalen van de zogenaamde kinetische fractienatie factor. Deze factor is theoretisch vast te stellen. De kinetische fractienatie factor i.e. de scheiding van isotopen in een molecuul. Knudsen diffusie is i.e. diffusie bij lage druk en een hoge gemiddelde vrije weglengte. Deze kinetische fractienatie factor wordt bepaald voor gassen als  $CO_2$ ,  $N_2O$  en  $O_2$ . Er is gekozen voor metingen onder de omstandigheden van Knudsen diffusie, omdat hier een duidelijke theorie voor is waardoor de resultaten uit het experiment direct gekoppeld kunnen worden aan de theorie. Aan mij de taak om het experiment te verbeteren aan de hand van de resultaten die geboekt worden. Er zijn al experimenten gedaan met deze opstelling, maar er was een significant verschil tussen de meetresultaten en de theorie. Er zal met een massaspectrometer analyses worden uitgevoerd wat betreft de verrijking van de isotopen. Er komt in de loop van mijn stage een nieuwe massaspectrometer, de universiteit van Utrecht is een van de eerste instellingen die deze massaspectrometer krijgt. Het uiteindelijke doel voor de universiteit is het kalibreren van deze massaspectrometer met mijn resultaten.

#### В **Viscous flow**

The following equations are used to calculate the viscous flow.

$Q_t = \frac{Z \cdot \Delta t}{N_A} \cdot V_m$		(21) (Linde, 2015)
with:		
$Q_t$	flow rate of the gas	(L/h)
Ζ	collision frequency	(s <sup>-1</sup> )
$\Delta t$	diffusion for 1 hour (3600)	(s)
N <sub>A</sub>	Avogadro's constant (6.022·10 <sup>23</sup> )	(mol <sup>-1</sup> )
$V_m$	molar volume at 296 K (24.5)	(L/mol).

From equation 1 only the collision frequency is unknown. The collision frequency can be written as:  $Z = \frac{1}{2} \cdot n \cdot v_x \cdot A$ (22) (Linde, 2015)

with:		
n	amount of molecules per volume-unit	(m⁻³)
$V_X$	velocity in the x-direction	(m·s⁻¹)
Α	area of the orifice	(m²).

From equation 2, *n* and  $v_x$  are unknown. However both *n* and  $v_x$  can be rewritten. First *n* will be taken into account, rewriting *n* gives:

$n = \frac{N}{V}$		(23) (Linde, 2	015)
with:			
Ν	amount of molecules	(-)	
V	volume of the gas	(L).	

The ideal gas law can be rearranged in order to determine the amount of molecules per volume area (n):

$P \cdot V = N \cdot K_B$	$T \to n = \frac{N}{V} = \frac{P}{K_B \cdot T}$	(2	24)
with:			
K <sub>B</sub>	Boltzmann constant (1.381·10 <sup>-23</sup> )	(J·K⁻¹)	
Ρ	the pressure within the set-up	(Pa)	
Т	temperature	(K).	

The velocity of	a gas can be determined from the kinetic ener	gy E <sub>kin</sub> :	
$E_{kin} = \frac{3}{2}K_BT =$	$=\frac{1}{2}mv^2$		(25)
with:	-		
т	mass of the molecule	(g)	
ν	velocity of the molecules in all directions	(m/s)	
E <sub>kin</sub>	kinetic energy of the molecules	(J).	

For the diffusion through an orifice, only the velocity in x-direction is considered. Therefore an estimation of  $v_x$  is:

$$\frac{1}{2}mv_x^2 \approx \frac{1}{2}K_BT \to v_x \approx \sqrt{\frac{K_BT}{m}}$$
(26) (Linde, 2015)

Substituting equation 4 and 6 in equation 2 gives:

$$Z = \frac{1}{2} \cdot \frac{P}{K_B \cdot T} \cdot \sqrt{\frac{K_B T}{m}} \cdot A = \frac{P \cdot A}{2 \cdot \sqrt{K_B \cdot T \cdot m}}$$
(27) (Linde, 2015)

The pressure is dependent on the amount of gas injected into the system. The total volume of the set-up is 5 L. To determine the pressure caused by the injected gas, the following equations will be used:

 $P = \frac{V_{injected}}{V_{reservoir}} \cdot 10^{5}$ (28) (Linde, 2015)  $V_{injected}$ amount of injected gas (SATP)
(mL)

 $v_{reservoir}$  total volume of the set-up (SATP) (5000) (mL).

Equation 1 can be solved as it contains known values. When the flow rate is known, the expected volume is dependent on the waiting time, shown in the following equation:

V <sub>diffused</sub>	$= \frac{2 \cdot \Delta t}{N_A} \cdot N_h \cdot V_m \cdot t_{wait}$		(29) (Linde, 2015)
with:			
$V_{diffused}$	volume of the diffused gas (SATP)	(L)	
t <sub>wait</sub>	time waited for the gas to diffuse	(s)	
N <sub>h</sub>	amount of holes in the foil	(-).	

### **C** Rayleigh equations

$$\delta_{x} = \left(\frac{R_{x}}{R_{inital}} - 1\right) \cdot 1000$$
(16)  
with  
 $R_{initial}$  ratio heavier to lighter isotope in initial gas (-).  
The Rayleigh equations are as follows:  
 $R_{residue} = R_{initial} \cdot f^{a-1}$ (18)  
with  
 $R_{residue}$  ratio heavier to lighter isotope in residue gas (-)  
 $\alpha$  the fractionation factor (-).  
Equation applies for the residue sample, new for the diffused sample:

Equation applies for the residue sample, now for the diffused sample:

 $R_{diffused} = R_{initial} \cdot \frac{1 - f^{\alpha}}{1 - f}$   $R_{diffused}$  ratio heavier to lighter isotope in diffused gas (-). (19)

As the results from the mass spectrometer are in  $\delta$ -values it is necessary to rewrite equation 18 and equation 19 in a form which contains the  $\delta$  value. This is carried by substituting equation 16 in equation 18 and in equation 19. For the residue side:

$$\begin{split} \delta_{residue} &= \left(\frac{R_{residue}}{R_{inital}} - 1\right) \cdot 1000\\ R_{residue} &= R_{initial} \cdot \left(\frac{\delta_{residue}}{1000} + 1\right) = R_{initial} \cdot f^{a-1}\\ &\left(\frac{\delta_{residue}}{1000} + 1\right) = f^{a-1}\\ &\frac{\delta_{residue}}{1000} = f^{a-1} - 1\\ &\delta_{residue} = (f^{\alpha-1} - 1) \cdot 1000 \end{split}$$

$$\delta_{residue} = (f^{\alpha - 1} - 1) \cdot 1000$$

(20)

For the diffused side a similar approach is applicable:

$$\delta_{diffused} = \left(\frac{R_{diffused}}{R_{inital}} - 1\right) \cdot 1000$$

$$R_{diffused} = R_{inital} \cdot \left(\frac{\delta_{diffused}}{1000} + 1\right) = R_{inital} \cdot \frac{1 - f^{\alpha}}{1 - f}$$

$$\left(\frac{\delta_{diffused}}{1000} + 1\right) = \frac{1 - f^{\alpha}}{1 - f}$$

$$\frac{\delta_{diffused}}{1000} = \frac{1 - f^{\alpha}}{1 - f} - 1$$

$$\delta_{diffused} = \left(\frac{1 - f^{\alpha}}{1 - f} - 1\right) \cdot 1000$$

$$\delta_{diffused} = \left(\frac{1 - f^{\alpha}}{1 - f} - 1\right) \cdot 1000$$
(21).

40



Figure 28. The change of the isotopic composition of  $\delta^{13}$ C in CO<sub>2</sub>



Figure 29. The change of the isotopic composition of  $\delta^{18}$ O in CO<sub>2</sub>

### D The pressure sensor

In the set-up, on the diffused side, a Balzers PKR-250 (See figure below) pressure sensor was used. This pressure sensor is an old type, Balzers is now Pfeiffer. These pressure sensors contain 2 measuring methods. A cold cathode method and Pirani measurements. The Pirani system is always running and the cold cathode system starts at a pressure of  $10^{-2}$  mbar.



Figure 30. Used pressure sensor on the diffusion set-up.

The principle of the Pirani system is a heated wire loses its heat due to collisions with molecules. When the amount of molecules (and thus the amount of collision) decreases, the heat loss will decrease, this way it can be related to the pressure in the system it is mounted on. (Indirect-gas-dependent pressure measurement, 2016) The cold cathode system basically contains two electrodes (Anode and Cathode with a high voltage in between). Negatively charged electrons are emitted from the cathode to the anode. While traveling to the anode these electrons ionize neutral molecules, located between the two electrodes. This causes a gas discharge which is a measure for the vacuum. (Ideal Vacuum products, 2016)

When during the experiments the set-up was evacuated (to  $10^{-5}$  mbar) and the valve to the vacuum pump was closed, the pressure increased to  $10^{-2}$  mbar and remained stable from that point on. From this observation it was concluded that the pressure sensor was the cause of the leak. Replacing the pressure sensor solved the leak.

### E statistical methods

For the thesis multiple statistical methods are applied. In this appendix the principle of these methods are explained. To calculate the error in the fraction of gas (*f*), the error in the calibration graph was established. This was established by calculating the error in the slope. This is done by Excel using the least squares method. The least squares method is essentially a method to fit the best linear curve through the data. (Shafer & Zhang, 2012)

For the error calculated in the  $\delta$  values the standard deviation is used and additionally the Students t-distribution. The equation for the standard deviation is as follows:

$$\sigma_n = \sum_{i=1}^n \frac{x_i - \mu}{n}$$

Due to the fact that the amount of data is not sufficient, the t-distribution is introduced. The tdistribution is based on the degrees of freedom (i.e. the amount of samples). To get the reliability of the samples up to 90%, the standard deviation has to be multiplied with the value that corresponds with the degrees of freedom. The next figure illustrates the t-distribution.



Figure 31. Student t-test. Various amounts of degrees of freedom plotted. If the degrees of freedom reach infinitival, the t-distribution will be equal to the normal-distribution. (Shafer & Zhang, 2012)

The notation of the student's t-distribution is as follow: SE·t0.95 This means that the standard deviation is multiplied with the corresponding t-value for a 95% confidence limit.