COMPUTATIONAL APPROACH TO THE EXPERIMENTAL DETERMINATION OF DIFFUSION COEFFICIENTS FOR OXYGEN AND NITROGEN IN HYDRAULIC FLUIDS USING THE PRESSURE-DECAY METHOD

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ABSTRACT

In the presented paper, the applicability of pressure-decay methods to determine the diffusivities of gases in hydraulic fluids is analysed. First, the method is described in detail and compared to other measurement methods. Secondly, the thermodynamics and the mass transfer process of the system are studied. This results in four different thermodynamic models of the gaseous phase in combination with two diffusion models. Thirdly, the influence of the models on the pressure-decay method is evaluated computationally by examining the diffusion process of air in water as all system parameters are available from literature. It is shown that ordinary pressure-decay methods are not applicable to gas mixtures like air and therefore a new method for calculating the diffusivities is suggested.

Keywords: Diffusivity, Pressure-decay method, Binary and ternary diffusion, Virial equation of state

1. INTRODUCTION

At all times in hydraulic systems a certain amount of air is present. It takes the form of entrained gaseous bubbles as well as dissolved air. Entrained air increases the risk of cavitation damage and reduces the effective bulk modulus of the fluid [1]. Dissolved air normally has no effect on the properties of the fluid but under certain circumstances it can outgas and increase the amount of entrained air in the system [1,2]. Therefore, it is of interest to determine the amount of dissolved air as well as the speed of the diffusion process.

The amount of gas solved in an ideal dilute solution is dependent on Henry's law constant and the partial pressure of the gas [3] given by equation (1):

$$x_i'' \cdot p'' = H_{ik} \cdot x_i' \quad (1)$$

In hydraulics, the Bunsen absorption coefficient is often used instead and is given by equation (2):

$$\alpha_i = \frac{(V_i')_S}{(V_k')_S} \cdot \frac{(p)_S}{p_i''} \quad (2)$$

The speed of the diffusion process depends on the diffusivity of the considered system. For binary system the diffusion process is governed by Fick's 2nd law of diffusion given by equation (3):

$$\frac{\partial C_i'}{\partial t} = D_{ik} \cdot \frac{\partial^2 C_i'}{\partial x^2} \quad (3)$$

Diffusion processes involving more than two solutes can be modelled with the generalized Fick's law or the Maxwell-Stefan equations. Due to their ease of applicability, the Maxwell-Stefan equations are chosen in this research (4):

$$\sum_{j=1, j \neq i}^N \frac{x_i' \cdot x_j'}{D_{ij}} \left(\frac{j_i'}{C_i'} - \frac{j_j'}{C_j'} \right) = - \frac{\partial x_i'}{\partial x} \quad \forall i \quad (4)$$

Currently there is only limited data available for diffusion coefficients of gases in hydraulic fluids. In this paper the authors address the problems involved in estimating the diffusivities for high pressure systems for ideal and non-ideal gases and gas mixtures. The emphasis is placed on the diffusion of nitrogen and oxygen in hydraulic fluids at pressures up to 300 bar. Thus,

the theory of diffusion for binary as well as ternary systems is analysed and their applicability to high pressure conditions is discussed. The three questions to be answered by this paper are:

1. Which method is to be preferred to measure the diffusion coefficients of gases in hydraulic fluids?
2. Is it necessary to regard air as a real gas or can the assumption of an ideal gas be made?
3. Can changes in the molar fractions of the gaseous phase be neglected?
4. How can the diffusivity of oxygen be determined for hydrocarbon-based hydraulic fluids?

2. MEASUREMENT METHODS AND APPARATUS

Several measurement methods for determining the diffusion coefficients of gases in liquids exist, originating from the research of crude oil. The measurement methods are typically categorized into two groups: direct and indirect methods.

Direct methods require measuring concentration profiles of diffusing components in order to directly determine diffusion coefficients. These methods involve either highly error-prone sampling, especially under high pressures [4], or non-invasive analysis techniques, which are usually expensive and demanding, like nuclear magnetic resonance [5], computer-assisted tomography [6,7] or planar laser-induced fluorescence [8,9].

Indirect methods require the observation of phenomena which are influenced by diffusion in order to indirectly determine the diffusivities. Indirect methods include decreasing bubble size methods [10] and constant bubble size methods [11,12]. As the names indicate the volume of a gas bubble inside the liquid phase is observed. The size can be decreasing due to absorption and diffusion of the gas into the liquid phase or the size can be constant if an appropriate gas volume flow into the bubble is provided. Also, indirect methods exist, for which the gas and liquid phase are reversed and the volume [13] or shape [14] of a liquid drop in a gas atmosphere is analysed. Bubble and drop size methods are relatively fast (experimental time within hours) and only need small sample sizes. The drawbacks are the elaborate techniques to isolate and fix the bubbles and drops without deforming them. Similar to drop and bubble size methods are microfluidic

approaches in which the change of the interface due to swelling is observed [15].

Most widely used are pressure decay methods [16-22], which is the method of choice in this paper. The advantages of this method are its simplicity and applicability to wide ranges of temperatures and especially pressures. Furthermore, with the same method it is also possible to accurately determine the Bunsen absorption coefficient as shown by Rambaks et al. [23]. A picture of the apparatus is shown in **Figure 1**, the working principles are presented **Figure 2**.

A cylindrical measurement chamber is partially filled with a specified volume of hydraulic fluid and connected to a compressed air bottle. With time nitrogen and oxygen will dissolve into the hydraulic fluid until it is completely saturated. At this point in time thermodynamic equilibrium (State 0) is reached. Subsequently, the piston of the apparatus is used to compress the measurement chamber further to State 1. This is a non-equilibrium state, at which it is assumed that the diffusion process begins and persists until a new thermodynamic equilibrium has been reached in State 2. [23]

During the diffusion process, the amount of gas in the gaseous phase decreases due to the increased solubility of the liquid at higher pressures. Therefore, a drop in pressure over time is measured and used to calculate the diffusion coefficient.

Figure 1: Pressure-decay measurement apparatus

Figure 2: Working principle of the measurement system [23]

3. THERMODYNAMICS AND MASS TRANSFER

The diffusion process is governed either by Fick's 2nd law of diffusion for binary systems (3) or by the Maxwell-Stefan equations (4) if more than two species are involved in the diffusion process.

For binary systems the diffusivity of gases can be determined easily from the measured pressure-decay curves [16-22], however for some systems this approach is not applicable due to safety reasons. The prime example of this is the diffusion of oxygen in hydrocarbon-based hydraulic fluids, which poses ignition risks.

The diffusivity of oxygen in hydraulic fluids could be determined by examining the diffusion of air, but the pressure-decay curve does not provide information about the individual diffusivities of oxygen and nitrogen. To formulate a new method for estimating the diffusivities of individual gas species, different diffusion models are analysed in the following chapters. Prior to that the solubility of gases in liquids is discussed.

3.1. Solubility of gases in liquids

According to Lüdecke et al. [3], thermodynamic equilibrium of a two-phase closed system persists, if it is in mechanical (5), thermal (6) and its components are in chemical equilibrium (7).

$$p' = p'' \quad (5)$$

$$T' = T'' \quad (6)$$

$$\mu'_i = \mu''_i \quad \forall i \quad (7)$$

In an equilibrium state of the two-phase system, a certain amount of dissolved gas is present in the liquid phase. To calculate the initial values of the concentration of dissolved gas in the liquid phase, the Bunsen absorption coefficient (2) for each species of gas has to be determined.

In Rambaks et al. [23] a method to calculate the Bunsen absorption coefficient for gases at high pressures with the use of measurement data from the equilibrium states was presented. It was found that the Bunsen absorption coefficient (2) can be calculated by evaluating the change in mass of gas in the gaseous phase given by equation (8):

$$\alpha_i = (\Delta m_i)_{0 \rightarrow n} \cdot \frac{(R_i)_s \cdot (T)_s}{(p_i)_n \cdot (V_k)_s} \quad (8)$$

The equation for the change in mass of gas in the gaseous phase is dependent on the pressure and temperature range and if the gas is a single species gas or a gas mixture. The reader is referred to Rambaks et al. [23] for a detailed analysis.

3.2. Binary diffusion model of ideal single species gases

The principle of binary diffusion within the context of the apparatus is depicted in **Figure 3**. The process is governed by Fick's 2nd law of diffusion (3). The initial values for the concentration as well as appropriate boundary conditions must be specified to solve the partial differential equation given by (3).

Figure 3: Binary diffusion in measurement apparatus

According to Kratschun et al. [24] and Freudigmann et al. [25] in the timescale of short deviations from a thermodynamic equilibrium of the system the diffusion process is negligible. Consequently, this allows the assumption that during the compression from State 0 to State 1 diffusion is negligible, and that the diffusion process begins only when State 1 has been reached. Therefore, the initial values for species concentration within the liquid phase can be determined based on equation (9):

$$C_i'(x, t = 0) = \alpha_i \cdot \frac{(p'')_0}{\bar{R} \cdot (T)_s} \quad \forall x \in (0, L) \quad (9)$$

Because of the diffusion process, the amount of substance and, therefore, the pressure in the measurement chamber decreases. The relationship between pressure, volume, temperature and amount of substance can be described with the equation of state for an ideal single species gas given by equation (10):

$$p_i'' \cdot V'' = n_i'' \cdot \bar{R} \cdot T'' \quad (10)$$

The temporal change in the amount of substance in the gaseous phase can be expressed by taking the derivative of equation (10) with respect to time, resulting in equation (11):

$$\frac{dn_i''}{dt} = \frac{V''}{\bar{R} \cdot T''} \cdot \frac{dp_i''}{dt} \quad (11)$$

By constructing a control volume around the gaseous phase, the molar flux within the gaseous phase can be determined with equation (12):

$$j_i'' = -\frac{4}{\pi \cdot d^2} \cdot \frac{dn_i''}{dt} \quad (12)$$

With the use of a surface mass balance at the interface between the liquid and gaseous phase, the molar flux within the liquid phase is equal to the molar flux within the gaseous phase and can be expressed with expression (13):

$$j_i' = j_i'' \quad (13)$$

From equations (12) and (13) it can be derived, that the molar flux of dissolved gas within the liquid phase is given by equation (14):

$$j_i' = -\frac{4}{\pi \cdot d^2} \cdot \frac{dn_i''}{dt} \quad (14)$$

According to Fick's 1st law of diffusion, the molar flux is directly proportional to the diffusivity and the concentration gradient as given by equation (15):

$$j_i' = -D_{ik} \cdot \frac{\partial C_i'}{\partial x} \quad (15)$$

Equation (15) allows to define Neumann boundary conditions at both ends of the liquid phase. At the gas-liquid interface, no accumulation of substance is possible. Therefore, the concentration gradient at the interface can be expressed with equation (16):

$$\left. \frac{\partial C_i'}{\partial x} \right|_{x=0} = \frac{4}{\pi \cdot d^2 \cdot D_{ik}} \cdot \frac{dn_i''}{dt} \quad (16)$$

Besides the Neumann boundary condition (16), a Dirichlet boundary condition given by equation (17) is specified:

$$C_i'(x = 0, t) = \alpha_i \cdot \frac{p''(t)}{\bar{R} \cdot (T)_s} \quad (17)$$

At the liquid-piston interface, there is no molar flux present and consequently the Neumann boundary condition is given by equation (18):

$$\left. \frac{\partial C_i'}{\partial x} \right|_{x=L} = 0 \quad (18)$$

With equations (9), (16), (17) and (18) the transient diffusion equation (3) is fully defined and can be solved even analytically for certain cases [19].

3.3. Binary diffusion model of real single species gases

According to Lüdecke et al. [3], the ideal gas law is applicable only in small pressure and temperature ranges. To take these limitations into account, a real gas model must be used. For single species gases it is convenient to use the compressibility factor, which is readily available from literature (see Vasserman et al. [28]).

The compressibility factor describes, how much a real gas deviates from the behaviour of an ideal gas. It is given by equation (19):

$$z_i = \frac{p_i'' \cdot V''}{n_i'' \cdot \bar{R} \cdot T} \quad (19)$$

By using equation (19) and the chain rule, an expression for the temporal change in the amount of substance in the gaseous phase is found (20):

$$\frac{dn_i''}{dt} = \frac{V''}{\bar{R} \cdot T'' \cdot z_i''} \left(z_i'' - p'' \cdot \frac{dz_i''}{dp_i''} \right) \frac{dp_i''}{dt} \quad (20)$$

Because the measurements are taken at high pressures, this approach is necessary due to large deviations from the ideal gas law as can be seen in **Figure 4**.

3.4. Ternary diffusion model of ideal gas mixtures

In the previous sections the theory of binary diffusion was discussed. This theory is applicable if the diffusion process involves the solvent and only one solute from the gaseous phase. It cannot be applied if two or more solutes are involved in the diffusion process at the same time [27].

Air is a multicomponent gas mixture consisting primarily of nitrogen and oxygen. Additionally, other gases like argon, carbon dioxide, neon, helium, water vapour and methane can also be present [3]. As an approximation, air can be treated as a two-component gas mixture

consisting of nitrogen and oxygen. This approach is adopted as it significantly simplifies the model.

Because the diffusion process involves three components (ternary diffusion), the Maxwell-Stefan equations (4) must be used. Using relations for the concentration and molar fractions equation (4) is rearranged to give equation (21):

$$\sum_{j=1, j \neq i}^N \frac{x_j' \cdot j_i' - x_i' \cdot j_j'}{\mathfrak{D}_{ij}} = -C' \cdot \frac{\partial x_i'}{\partial x} \quad \forall i \quad (21)$$

According to Whitaker [27], for ideal dilute solutions the assumptions given by equation (22) can be made for a solvent k :

$$\begin{aligned} x_{N_2}' \rightarrow 0 &\Rightarrow C_{N_2}' \rightarrow 0 \\ x_{O_2}' \rightarrow 0 &\Rightarrow C_{O_2}' \rightarrow 0 \\ x_k' \rightarrow 1 &\Rightarrow C' = C_k' = \text{const.} \end{aligned} \quad (22)$$

These assumptions allow to simplify the Maxwell-Stefan equations to obtain expressions (23) and (24):

$$\frac{\partial C_{N_2}'}{\partial x} = -\frac{j_{N_2}'}{\mathfrak{D}_{N_2 k}} \quad (23)$$

$$\frac{\partial C_{O_2}'}{\partial x} = -\frac{j_{O_2}'}{\mathfrak{D}_{O_2 k}} \quad (24)$$

According to Bird et al. [26], the temporal changes of concentration in the liquid phase are governed by equations (25) and (26):

Figure 4: Compressibility factors for air [28]

$$\frac{\partial^2 C'_{N_2}}{\partial x^2} = -\frac{1}{D_{N_2k}} \cdot \frac{\partial j'_{N_2}}{\partial x} \quad (25)$$

$$\frac{\partial^2 C'_{O_2}}{\partial x^2} = -\frac{1}{D_{O_2k}} \cdot \frac{\partial j'_{O_2}}{\partial x} \quad (26)$$

By differentiating (23) and (24) with respect to x and by using equations (25) and (26) expressions for the transient diffusion of nitrogen and oxygen are obtained:

$$\frac{\partial C'_{N_2}}{\partial t} = D_{N_2k} \cdot \frac{\partial^2 C'_{N_2}}{\partial x^2} \quad (27)$$

$$\frac{\partial C'_{O_2}}{\partial t} = D_{O_2k} \cdot \frac{\partial^2 C'_{O_2}}{\partial x^2} \quad (28)$$

As can be observed from expressions (27) and (28), the complex Maxwell-Stefan equations reduce to two equations of binary diffusion. The reason for this is the assumption of an ideal dilute solution in which interactions between the solutes do not occur [26]. These assumptions are only possible because the concentration of solvent is almost unity compared to the concentration of the gases to be dissolved. In other words, due to the low solubility of the air's components the Maxwell-Stefan equations converge to Fick's 2nd law but for oxygen and nitrogen separately.

If the diffusivity is to be measured at moderate pressures and temperatures, the ideal gas mixture model can be used. Then, using Dalton's law the temporal changes in the amount of substance of nitrogen and oxygen can be expressed with equations (29) and (30):

$$\frac{dn''_{N_2}}{dt} = \frac{V''}{\bar{R} \cdot T''} \cdot \frac{dp''_{N_2}}{dt} \quad (29)$$

$$\frac{dn''_{O_2}}{dt} = \frac{V''}{\bar{R} \cdot T''} \cdot \frac{dp''_{O_2}}{dt} \quad (30)$$

3.5. Ternary diffusion model of real gas mixtures

When considering the solubility of a real gas mixture, the fugacity coefficient has to be taken into account due to the non-ideal behaviour of the gaseous phase [3]. Hence, equation (1) is rewritten to equation (31):

$$x''_i \cdot \varphi_i \cdot p'' = H_{ik} \cdot x'_i \quad \forall i \quad (31)$$

According to Lüdecke et al. [3], multiple equations of state can be used to calculate the

fugacity coefficient of each gas species. In this paper, the virial equation of state with 3 coefficients is chosen and is given by expression (32):

$$p'' \cdot v''_m = \bar{R} \cdot T'' \cdot \left(1 + \frac{B}{v''_m} + \frac{C}{v''_m{}^2} \right) \quad (32)$$

The equation for the fugacity coefficient is given by equation (33):

$$\begin{aligned} \ln(\varphi_i) = & \frac{2}{v''_m} \sum_{j=1}^N x''_j B_{ij} - \ln(z) \\ & + \frac{3}{2v''_m{}^2} \sum_{j=1}^N \sum_{k=1}^N x''_j x''_k C_{ijk} \end{aligned} \quad (33)$$

Using equation (31) the necessary Dirichlet boundary condition for each species of gas can be calculated with expression (34):

$$x'_i(x=0, t) = \frac{x''_i \cdot \varphi_i \cdot p''}{H_{ik}} \quad (34)$$

The pressure-decay method allows to calculate the diffusivity of pure gases, however the diffusivity of oxygen cannot be determined in this way due to ignition risks. Therefore, the authors propose a new approach:

1. Calculate the diffusivity of pure nitrogen;
2. Measure the pressure-decay for air;
3. Determine the diffusivity of oxygen from the pressure-decay curve for air with computational simulations using the ternary diffusion model of real gas mixtures.

4. COMPUTATIONAL ANALYSIS

To demonstrate the discrepancies between the different thermodynamic and diffusion models, simulations were conducted using a finite difference scheme. The liquid domain is discretised and an explicit Euler approach is chosen to calculate the concentration within it over time. The test case considered is the diffusion of nitrogen and oxygen in water, since the values for diffusivities and Henry coefficients are readily available. Also, the thermophysical properties of air are well documented by Vasserman et al. [28].

The single species real gas model was used to calculate the pressure-decay for nitrogen and oxygen separately. The two curves provide an

upper and lower bound for the pressure-decay curves of the ternary diffusion models.

The parameters for the diffusivities, Henry coefficients and virial coefficients are presented in **Table 1**:

Table 1: Diffusivities, Henry and virial coefficients

Diffusivities of system	Value [m ² /s]
Diffusivity $D_{N_2H_2O}$	2.000×10^{-9}
Diffusivity $D_{O_2H_2O}$	2.420×10^{-9}
Henry coefficients	Value [Pa]
Henry coefficient $H_{N_2H_2O}$	8.59×10^9
Henry coefficient $H_{O_2H_2O}$	4.42×10^9
Virial coefficients	Value [m ³ /mol]
Coefficient $B_{N_2N_2}$	-4.34×10^{-6}
Coefficient $B_{N_2O_2}$	-9.70×10^{-6}
Coefficient $B_{O_2O_2}$	-15.96×10^{-6}
Virial coefficients	Value [m ⁶ /mol ²]
Coefficient $C_{N_2N_2N_2}$	1.90×10^{-9}
Coefficient $C_{N_2N_2O_2}$	1.50×10^{-9}
Coefficient $C_{N_2O_2O_2}$	0.39×10^{-9}
Coefficient $C_{O_2O_2O_2}$	35.00×10^{-12}

The parameters of the measurement chamber are listed in **Table 2**:

Table 2: Dimensions of measurement chamber

Chamber parameters	Value [mm]
Initial gaseous phase height h_0''	10.0
Initial liquid phase height h_0'	150.0
Piston diameter d	65.0

The system is considered isothermal at a temperature of 303.15 K. The initial molar fractions in the gaseous phase are 79.38% nitrogen, 20.62% oxygen for the ternary systems. Because the solvent in this test case is water, water vapour is formed in the gaseous phase and must be considered. The values for the initial pressure (State 0), the intermediate pressure (State 1) and the saturation pressure of water [29] are given in **Table 3**:

Table 3: Values for pressure

Chamber pressures	Value [bar]
Initial pressure p_0''	50.0
Intermediate pressure p_1''	300.0
Saturation pressure of water $p_{H_2O}^s(@303.15 K)$	42.47×10^{-3}

The molar fraction of water in the gaseous phase can be determined with Raoult's law (35):

$$x_{H_2O}''(x_{H_2O}' \rightarrow 1) = \frac{x_{H_2O}' \cdot p_{H_2O}^s(303.15 K)}{p_0''} \quad (35)$$

The values of the molar fractions of water in the gaseous phase at 1.0 bar, in State 0 and in State 1 are given in **Table 4**:

Table 4: Values for molar fraction of water in air for system air-water

Molar fractions of water	Value [-]
Molar fraction $x_{H_2O}''(@1 bar)$	42.47×10^{-3}
Molar fraction $x_{H_2O}''(@50 bar)$	8.49×10^{-4}
Molar fraction $x_{H_2O}''(@300 bar)$	1.42×10^{-4}

As can be seen, the water vapour content is significant only at ambient pressure. At higher pressures it is negligible compared to the content of nitrogen and oxygen. Even more interesting is that by considering this test case an upper bound for the molar fraction of water vapour in the gaseous phase is found for all other liquid-air systems.

When considering other fluids, e.g. hydraulic fluids, where the water content in the liquid phase is unknown, the limiting case of Raoult's law (35) for the water-air system is very convenient to use. Applying it to other systems is equivalent to having a relative humidity of 100% of the gaseous phase. Therefore, if in the limiting case given by (35) the molar fraction of water vapour is already negligible, it is also negligible for any other case.

With the given parameters it is possible to simulate the diffusion process and express the pressure in the measurement chamber as a function of time. A comparison between the pressure curves is given in **Figure 5**. As mentioned before the pressure-decay curves of pure nitrogen and pure oxygen provide an upper and lower bound for the ternary model.

As shown, the pressure curves for the ideal and real gas mixture models differ for the given parameters by a maximal value of approximately 10 bar (@190 h). Once thermodynamic equilibrium is reached, the discrepancy is approximately 5 bar. Keeping in mind that the pressure-decay within the measurement chamber is recorded over time, differences in the pressure curves will lead to different values for the diffusivities.

Another observation is depicted in **Figure 6**. Due to the different solubilities of nitrogen and oxygen in water, the molar fraction of nitrogen in the gaseous phase increases while that of oxygen decreases compared to their respective initial values as was already noted by Rambaks et al. [23].

A closer inspection of **Figure 6** reveals that the molar fraction of nitrogen reaches a maximum value and then starts to decrease. The larger diffusion coefficient of oxygen is the most likely explanation for this observation.

The change in gaseous phase composition has a direct effect on the calculation of the diffusivities. This is most notable in equation (33) for the fugacity coefficients and in the expressions for the Dirichlet boundary conditions (34).

Figure 5: Pressure-decay over time for diffusion in water

Figure 6: Molar fraction of nitrogen over time for diffusion in water

5. OPERATIONAL TESTING

To test the functionality of the apparatus, a test-run with water and air at low pressure was conducted for a period of 200 hours. The measured pressure-decay curve is shown in **Figure 7**.

The goal of this test was to determine, if the system converges to a state of thermodynamic equilibrium. This would indicate, that the apparatus is leak-proof.

The diffusion process was accelerated with the use of a magnetic stir bar, which was placed in the measurement chamber and activated in the 12th hour of the test. As can be observed, this leads to an immediate decrease in pressure. Following this rapid decrease, it was switched off for 10 hours and activated again within the 22nd hour of the test. Once more, an acceleration of the diffusion process can be noted.

With time the gradient of the pressure-decay curve flattens out as depicted in **Figure 7**. This indicates, that the diffusion process is slowing down and converging to thermodynamic equilibrium. Based on this it can be said, that the measurement apparatus is leak-proof.

From the first 12 hours of testing the resulting preliminary pseudo-diffusivity of air in water is determined to be $D = 1.1 \times 10^{-9} \text{ m}^2/\text{s}$. This value is of the same magnitude as the diffusivities of nitrogen and oxygen.

6. CONCLUSION AND OUTLOOK

In the presented paper different methods for determining the diffusivities of nitrogen and oxygen in liquids were discussed. Among these methods the pressure-decay method was chosen as the best suited for hydraulic fluids. A measurement apparatus and its working principles were described along with the design aspects and the operating procedure.

It was shown, that for high pressure diffusion a real gas mixture model has to be used due to the non-ideal behaviour and the changing composition of the gaseous phase. The numerical results reveal that it is necessary to capture these effects when applying the pressure decay method to gas mixtures because otherwise one cannot determine the individual diffusivities and because the non-ideal behaviour introduces severe deviations compared to the ideal gas mixture model, especially if the measurement time is limited to 10 days (240 hours) or less.

The described apparatus has been set up, tested and measurements of the diffusivities are subject to current research at ifas.

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Figure 7: Measured pressure-decay over time for diffusion of nitrogen and oxygen in water

NOMENCLATURE

B	2 nd Virial coefficient
C	Concentration / 3 rd Virial coefficient
d	Piston diameter
D	Diffusion coefficient
$\mathcal{D}$	Maxwell-Stefan-diffusion coefficient
h	Height
H	Henry coefficient
i	Index
j	Index / Molar flux
k	Index
L	Length
m	Mass
n	Index / Amount of substance
N	Index
p	Pressure
R	Specific gas constant
$\bar{R}$	Universal gas constant
S	Standard reference conditions / Saturation
t	Time
T	Temperature
v_m	Molar Volume
V	Volume
x	Coordinate / Molar fraction
z	Compressibility factor
α	Bunsen absorption coefficient
μ	Chemical potential
φ	Fugacity coefficient
'	Liquid phase
"	Gaseous phase

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