

Protocol of experiment
EFFECTIVE DIFFUSION COEFFICIENT

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Experiment conducted on May 13th 2005

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1 Description of the experiment

Goal of the experiment is to determine an effective diffusion coefficient D_{12}^e in a porous catalyst out of the measurement of concentration over time ($\frac{dc}{dt}$). By knowing the molecular diffusion coefficient D_{12} it is possible to calculate the tortuosity τ , which is a dimension, that represents the ratio of a real distance to the shortest possible distance.

1.1 Experimental set-up and procedure

The rig for the experiment is structured as follows:

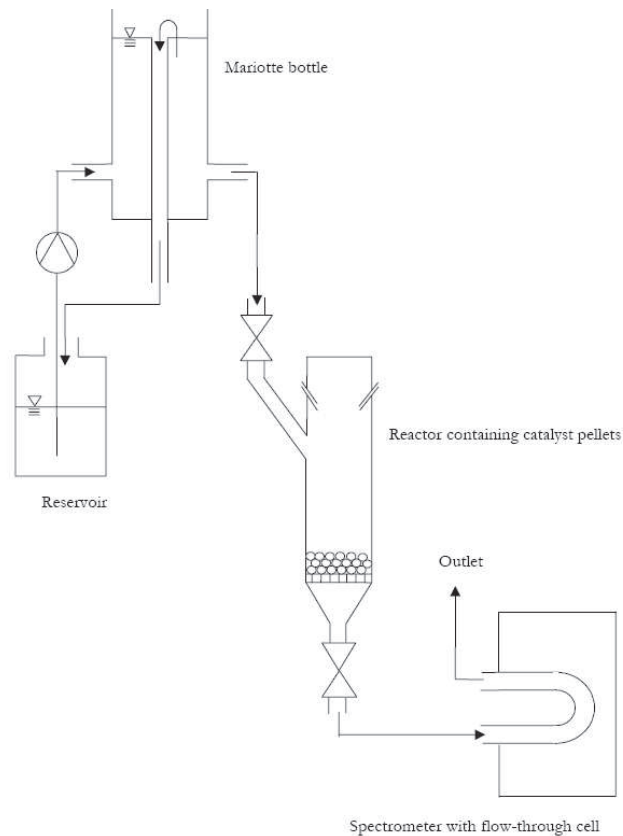


Figure 1: Experimental set-up [1]

First a constant volume flow of the Methanol-Water-Mixture, which has to be freshly prepared, is assured. Every catalyst pellet is measured by a micrometer and the results are written down.

All the pellets are put into benzoic acid, which acts as the tracer, that is to be measured by the UV-Vis spectrometer.

In order to remove all air bubbles from the pellets, vacuum from a water-jet pump is applied in a desiccator. The vacuum procedure is to be applied twice.

It is very important for carrying out the experiment, that no benzoic acid is left on the outer surface of the pellet. So the pellets are shuttled on a sheet of paper for some time.

Finally the pellets are filled into the reactor and the flux of methanol-water is turned on.

Now the UV-Vis spectrometer measures the extinction of the sample every 0.3 s. The experiment

is done after 1024 values have been recorded (approx. 5 minutes). Then the data is transferred to a computer.

2 Measured values

2.1 Experimental conditions

Three different types of catalyst pellets were used:

Catalyst	SA 5205		
Test run	No. 1	No. 2	No. 3
Porosity ε	0.49 to 0.55, average 0,47		
Specific surface S_M [m^2/g]	0.005 to 0.50, average 0.25		
Mean diameter \bar{d}_K [mm]	4.3	5.1	5.0

Table 1: Parameters for catalyst SA 5205

Catalyst	SA 5252		
Test run	No. 1	No. 2	No. 3
Porosity ε	0.51 to 0.60 average 0,56		
Specific surface S_M [m^2/g]	0.20 to 0.50, average 0.35		
Mean diameter \bar{d}_K [mm]	5.1	5.1	4.7

Table 2: Parameters for catalyst SA 5252

Catalyst	DU 460/1/9			
Test run	No. 1	No. 2	No. 3	No. 4
Porosity ε	0.48			
Mean diameter \bar{d}_K [mm]	2.8	2.6	2.7	2.5

Table 3: Parameters for catalyst DU 460/1/9

2.2 Measured data

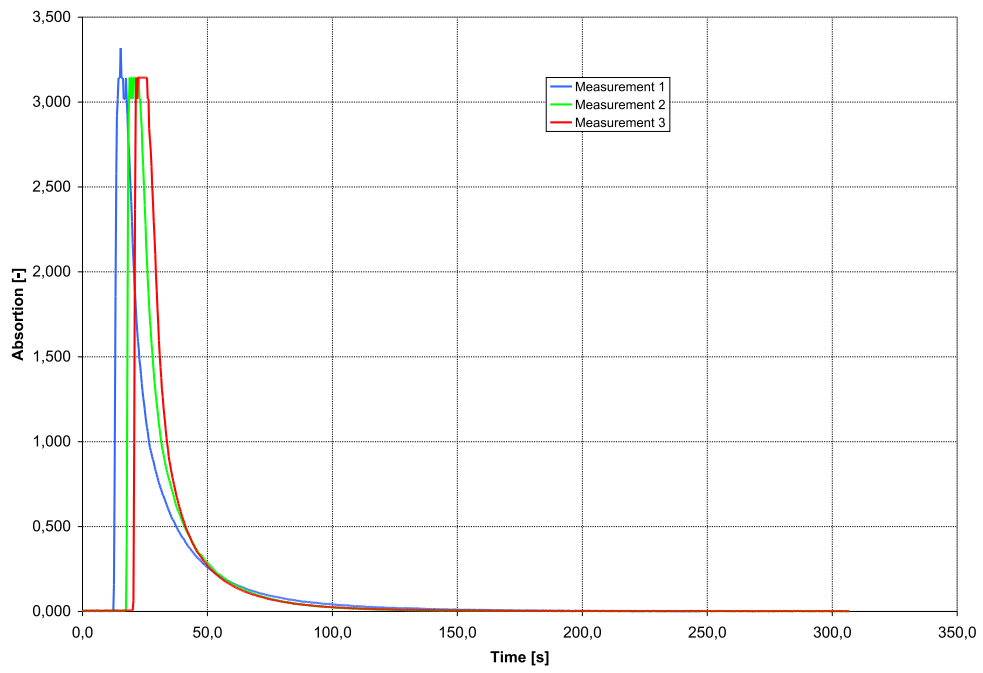


Figure 2: SA5205 Data

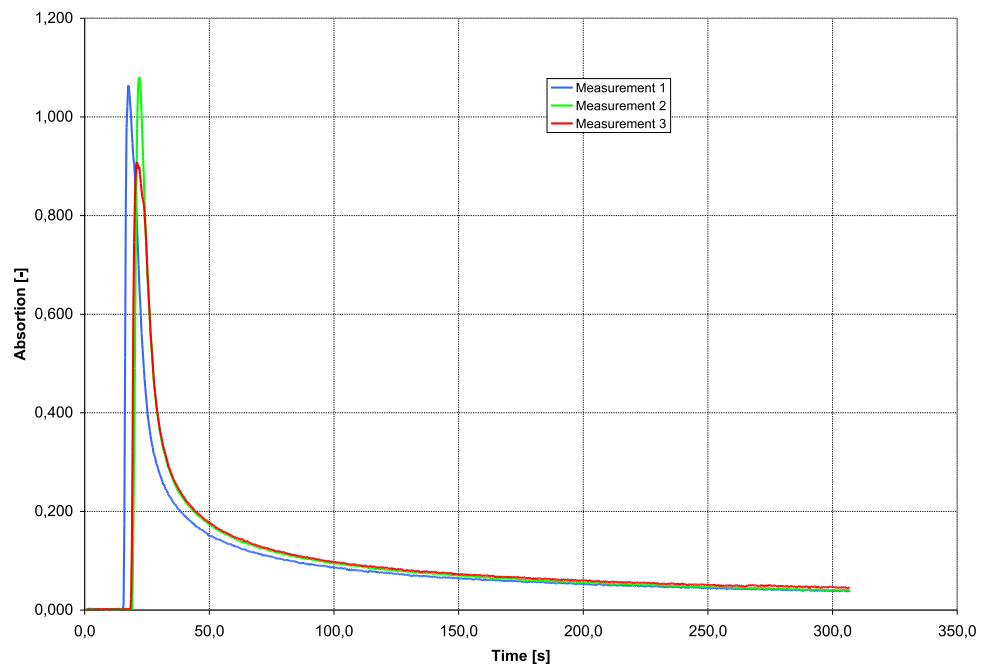


Figure 3: SA5252 Data

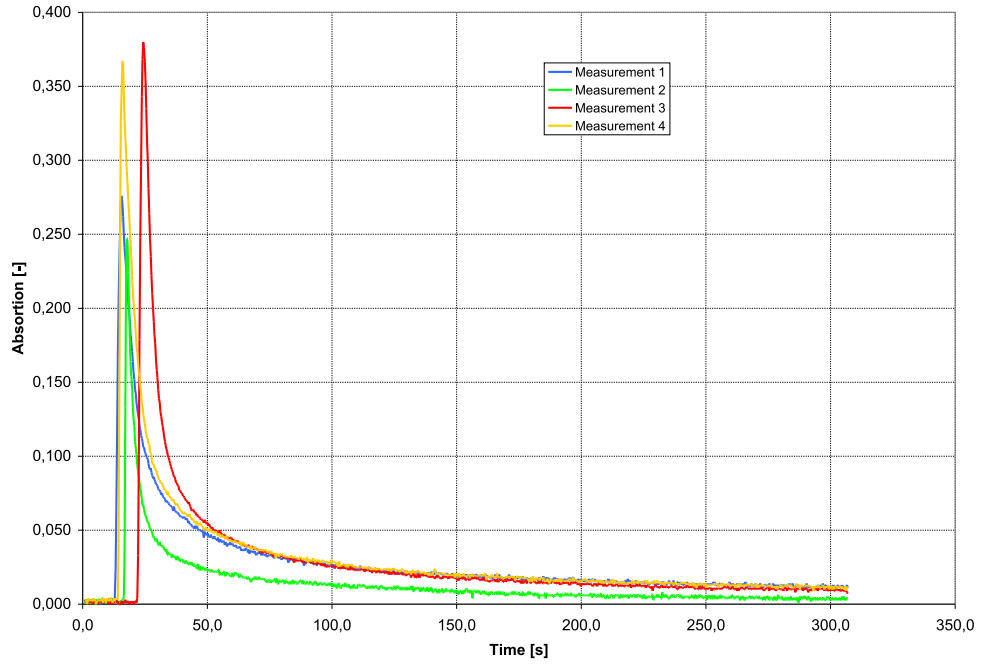


Figure 4: DU 46019 Data

3 Results

3.1 Derivation of FICK's 2nd Law

3.1.1 General form

Depending on the way shown in [5, p. 818], FICK's 2nd Law can be derived as follows.

Considering a non stationary situation in a system, the change of concentration by means of time are important. To analyse this, we observe the number of molecules in an infinitesimal volume element $dV = A dz$ at different times. This number N in dV is a concentration c .

In case, that the in-flux $\left. \frac{dc}{dt} \right|_{z_0}$ and out-flux $\left. \frac{dc}{dt} \right|_{z_0-dz}$ of molecules in this control volume are different, the concentration $\left. \frac{dc}{dt} \right|_{dV}$ of this volume element is changing.

We define, that there is a gradient in concentration parallel to the z -Axis, so that with higher numbers of z , the concentration is higher. This result in a diffusion in direction to negative z values. Figure 5 illustrates this situation.

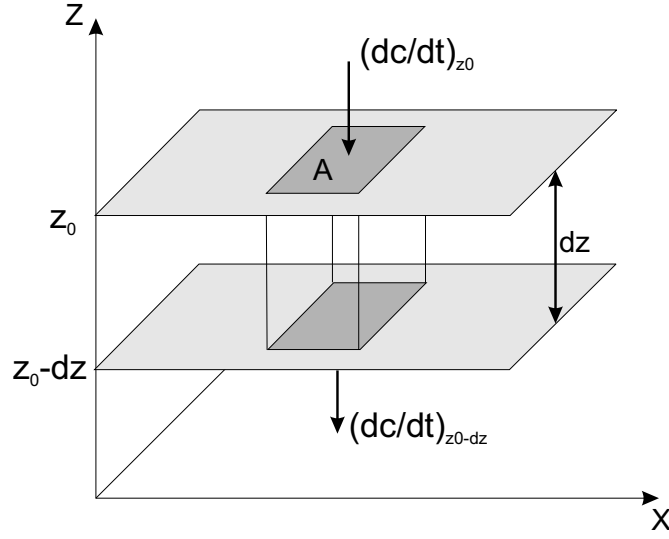


Figure 5: Definitions for Fick's 2nd Law

So the fortification of molecules in dV equals the difference between in-flux and out-flux velocity:

$$\left. \frac{dc}{dt} \right|_{dV} A dz = \left. \frac{dc}{dt} \right|_{z_0} - \left. \frac{dc}{dt} \right|_{z_0-dz} \quad (1)$$

A difference between in-flux and out-flux is not possible without a concentration gradient, so that

$$\left(\frac{dc}{dt} \right)_{z_0-dz} = \left(\frac{dc}{dt} \right)_{z_0} + \frac{d \left(\frac{dc}{dt} \right)_{z_0}}{dz} dz \quad (2)$$

Insertion of (2) in (1) gives

$$\frac{dc}{dt} a dz = \left(\frac{dc}{dt} \right)_{z_0} - \left[\left(\frac{dc}{dt} \right)_{z_0} + \frac{d \left(\frac{dc}{dt} \right)_{z_0}}{dz} dz \right] \quad (3)$$

$$A \frac{dc}{dt} = - \frac{d}{dz} \left[\left(\frac{dc}{dt} \right)_{z_0} \right] \quad (4)$$

Now, we can insert FICK's 1st Law:

$$\vec{J} = -D_{12} \frac{dc}{dz} \quad (5)$$

with

$$J = \frac{dc}{A dt} \quad (6)$$

into (4) and it follows:

$$A \frac{dc}{dt} = -A \frac{d}{dz} \left[-D_{12} \left(\frac{dc}{dz} \right) \right] \quad (7)$$

In case, that $D_{12} \neq f(z)$ (so that the diffusion coefficient is not changing with different values of z), (7) can be rewritten to

$$\frac{dc}{dt} = D_{12} \frac{d^2c}{dz^2} \quad (8)$$

(8) is known as FICK's **2nd Law**.

3.1.2 Special form for porous media

The general form does not take account, that there are pores.

$$V_{total} = A \cdot dz = \frac{V_{pore}}{\varepsilon} \quad (9)$$

Concentration is referred only to the liquid phase / pore volume:

$$c = \frac{n}{V_{pore}} = \frac{n}{V_{total}\varepsilon} = \frac{c_{total}}{\varepsilon} \quad (10)$$

Now we consider the situation in (8):

$$\underbrace{\frac{dc_{total}}{dt}}_{\text{complete}} = D_{12} \underbrace{\frac{d^2c}{dz^2}}_{\text{liquid phase as of FICK's 1st Law}} \quad (11)$$

and insert the conclusion of (10) ($dc_{total} = \varepsilon dc$)

$$\frac{dc}{dt} = \frac{D_{12}^e}{\varepsilon} \frac{d^2c}{dz^2} \quad (12)$$

3.2 Calculation of the molecular diffusion coefficient

It is not possible to calculate the molecular diffusion coefficient for liquids. But there exists an empirical equation for approximating the molecular diffusion coefficient in diluted solutions. It's based on WILKE and CHANG and taken from [2, equation 5.12]

$$D_{12} = 7.4 \cdot 10^{-8} \frac{T \left(X \cdot M_{H_2O/CH_3OH} \right)^{0.5}}{\mu \left(V_{C_6H_5COOH} \right)^{0.6}} \quad \left(cm^2 \cdot s^{-1} \right) \quad (13)$$

Hence the ratio of the solution of methanol and water is 1 : 9, the parameters are determined by means of mixing rule. These are the molecular weight (values taken from [3])

$$M_{H_2O/CH_3OH} = 0.9 \cdot 18.0153 \text{ g/mol} + 0.1 \cdot 32.0422 \text{ g/mol} = 19.4 \text{ g/mol} \quad (14)$$

the dynamic viscosity (dynamic viscosity for methanol taken from [6])

$$\eta_{H_2O/CH_3OH} = 0.9 \cdot 1.00 \text{ mPas} + 0.1 \cdot 0.52 \text{ mPas} = 0.95 \text{ mPas} \quad (15)$$

and the association factor (values taken from [2, page 70])

$$X_{H_2O/CH_3OH} = 0.9 \cdot 2.6 + 0.1 \cdot 1.9 = 2.53 \text{ mPas} \quad (16)$$

Further parameters are the temperature $T = 293.15 \text{ K}$ and the molar volume. To approximate the molar volume of benzoic acid we add the molar volumes of the atomic components after [2, tab. 5.3].

$$V_{C_6H_5COOH} = 7 \cdot 14.8 + 6 \cdot 3.7 + 2 \cdot 12.0 - 15.0 = 134.8 \text{ cm}^3/\text{mol} \quad (17)$$

With these values we obtain a molecular diffusion coefficient of $D_{12} = 8.424 \cdot 10^{-10} \text{ m}^2/\text{s}$.

3.3 Calculation of the effective diffusion coefficient

The result of the UV-Vis measurement are curves showing the absorption resp. the concentration against time. First the offset caused by noise has to be abstracted from the measurement values. Therefor the lowest value is abstracted. Now the first values which aren't part of the peak are erased. For the determining the effective diffusion coefficient some modifications have to be done. Due to non-ideal concentration leap of the signal the origin of coordinates is set in such a way that both shaded surfaces shown in figure 6 are equal.

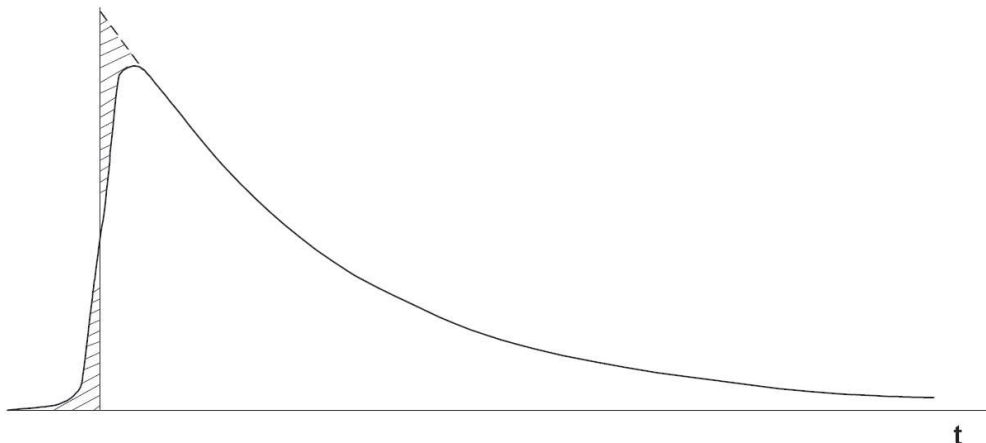
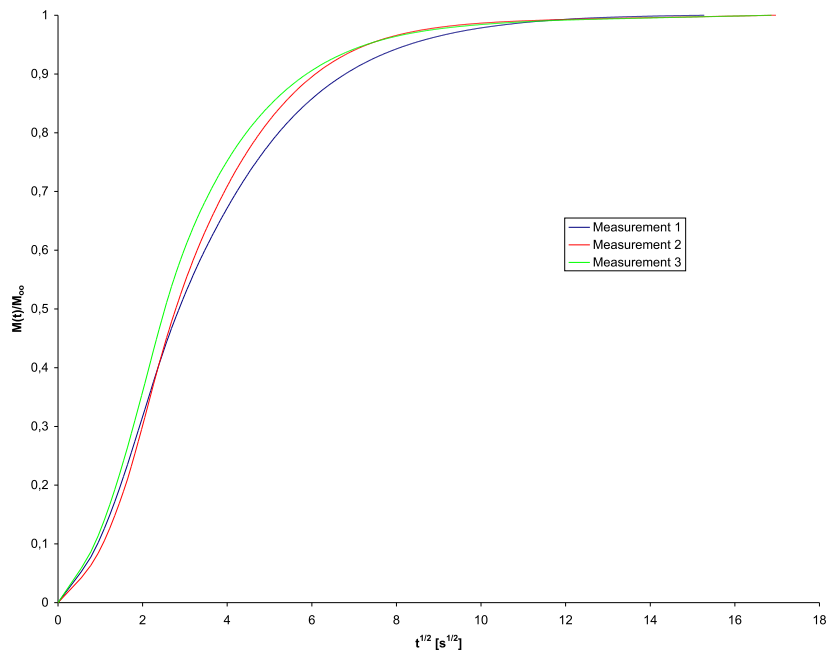
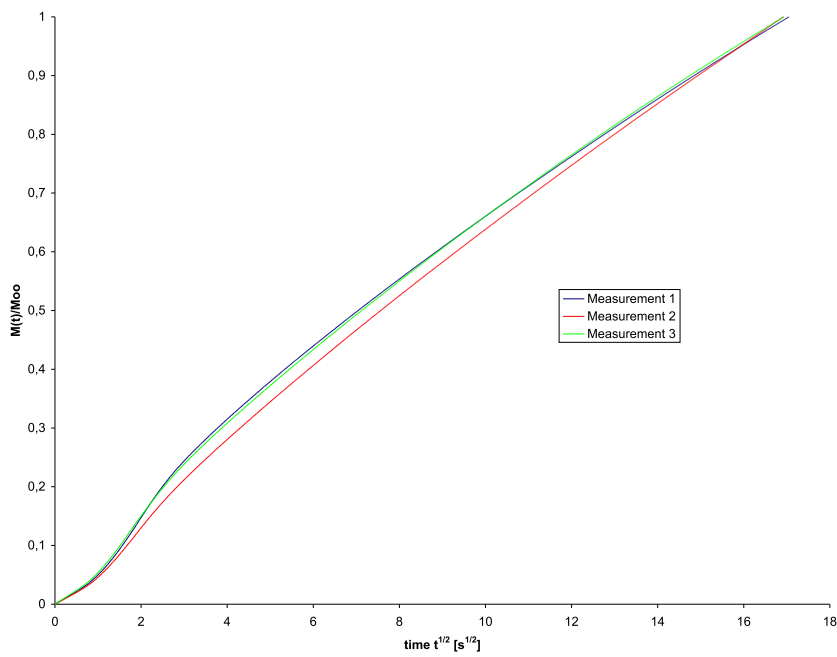


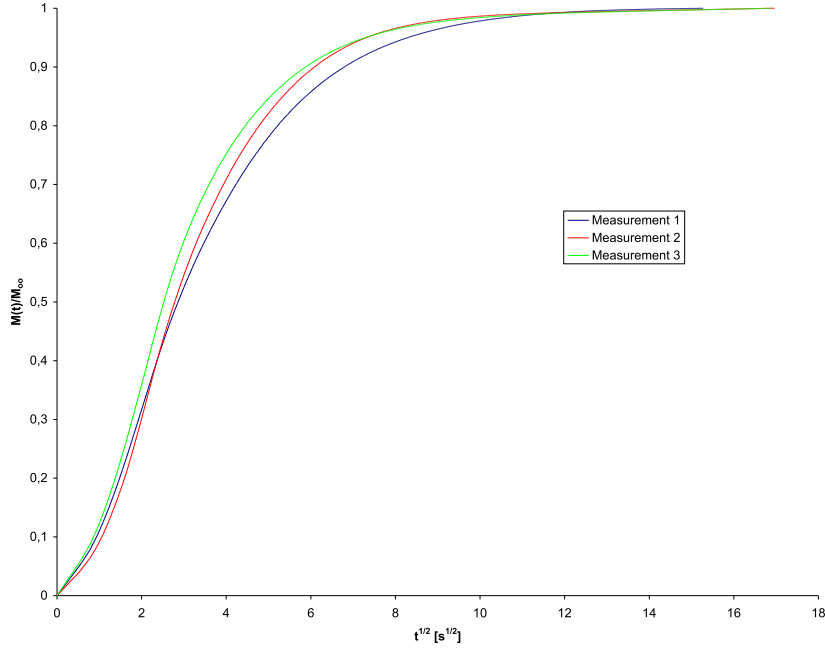
Figure 6: Correction of the UV-Vis-signal [1]

Therefor a linear trend line is put over the first five value pairs after peak maximum. The area between trend line and measurement curve as well as the area between curve and t-axis is calculated numerally by means of trapezoidal rule.

$$A = \frac{t_{i+1} - t_i}{2} \cdot (f(t_i) + f(t_{i+1})) \quad (18)$$

The t-value where both areas are approximately equal is the new origin. To yield the modified peaks the first measurement values until trend line subtends the measurement curve are substituted by the values of the trend line. The modified peaks are now integrated by means of trapezoidal rule as shown in equation 18. The amount of substance $M(t)$ extracted by diffusion until time t is obtained by integration between 0 and t . To normalize it to 1 $M(t)$ is divided by the total amount of substance M_∞ . Due to the numerally integration the value $M(t)/M_\infty$ for $t^{1/2} = 0$ doesn't equal 0 as it would be in case of analytical integration. Therefor the value $M(t)/M_\infty$ for $t^{1/2} = 0$ has to be set to 0 manually (see figure 11 on page 11). The relation $M(t)/M_\infty$ against $t^{1/2}$ is outlined in the following figures.

Figure 7: $M(t)/M_\infty - t^{1/2}$ Plot for SA-5205Figure 8: $M(t)/M_\infty - t^{1/2}$ Plot for SA-5252

Figure 9: $M(t)/M_\infty - t^{1/2}$ Plot for DU-46019

In order to determine the effective diffusion coefficient you need to know the slope for $t=0$. After [1, Equation 14]

$$\left. \frac{d \frac{M(t)}{M_\infty}}{d(\sqrt{t})} \right|_{t=0} = 6 \frac{\sqrt{\frac{D_{12}^e}{\varepsilon \pi}}}{\frac{d_K}{2}} \quad (19)$$

the effective diffusion coefficient is determined as

$$D_{12}^e = \frac{\pi \varepsilon d_K^2}{144} \cdot \left. \frac{d \frac{M(t)}{M_{infly}}}{d(\sqrt{t})} \right|_{t=0} \quad (20)$$

With the given parameters as shown in tables 1 to 3 on page 2 this leads to the following results.

Catalyst	SA 5205			
Test run	No. 1	No. 2	No. 3	
Slope for $t = 0$ [$s^{-1/2}$]	0.096	0.077	0.106	
E. Diff. Coeff. D_{12}^e [m^2/s]	$1.749 \cdot 10^{-9}$	$1.577 \cdot 10^{-9}$	$2.863 \cdot 10^{-9}$	
Catalyst	SA 5252			
Test run	No. 1	No. 2	No. 3	
Slope for $t = 0$ [$s^{-1/2}$]	0.096	0.077	0.106	
E. Diff. Coeff. D_{12}^e [m^2/s]	$5.721 \cdot 10^{-10}$	$6.986 \cdot 10^{-10}$	$4.225 \cdot 10^{-10}$	
Catalyst	DU 460/1/9			
Test run	No. 1	No. 2	No. 3	No. 4
Slope for $t = 0$ [$s^{-1/2}$]	0.039	0.071	0.055	0.049
E. Diff. Coeff. D_{12}^e [m^2/s]	$1.248 \cdot 10^{-9}$	$3.578 \cdot 10^{-9}$	$2.247 \cdot 10^{-9}$	$1.513 \cdot 10^{-9}$

Table 4: Results of effective diffusion coefficient for the catalysts

3.4 Calculation of the tortuosity

As in chapter 3.2 determined the molecular diffusion coefficient is $D_{12} = 8.424 \cdot 10^{-10}$. With [1, equation 3]

$$D_{12}^e = \frac{\varepsilon}{\tau} D_{12} \quad (21)$$

given the porosity ε (see tables 1 to 3 on page 2) and the experimentally determined effective diffusion coefficient D_{12}^e (see table 4 on the preceding page) we can now determine the tortuosity τ .

$$\tau = \frac{\varepsilon \cdot D_{12}}{D_{12}^e} \quad (22)$$

Catalyst	SA 5205			
Test run	No. 1	No. 2	No. 3	
Tortuosity τ	0.226	0.251	0.138	
Catalyst	SA 5252			
Test run	No. 1	No. 2	No. 3	
Tortuosity τ	0.817	0.669	1.107	
Catalyst	DU 460/1/9			
Test run	No. 1	No. 2	No. 3	No. 4
Tortuosity τ	3.241	1.130	1.800	2.673

Table 5: Tortuosity values for the catalysts

4 Evaluation of results and errors

4.1 Comparison of the results to literature values

According to [1] the magnitude of molecular diffusion coefficients within liquids is about $10^{-9} \text{ m}^2/\text{s}$. The molecular diffusion coefficient determined in chapter 3.2 is $8.424 \cdot 10^{-10}$. In consideration of equation (13) being empirical the deviation to literature values lies in an usual range. For a better comparison of effective diffusion coefficients they are outlined figure 10. After a rough estimation in [4, session 5b, page 5] the effective diffusion coefficient is about a tenth of the molecular diffusion coefficient. In case of catalyst SA 5205 the effective diffusion coefficient is larger than the molecular diffusion coefficient. This fact indicates an erroneous determination of effective diffusion coefficients. Indeed there are from the performance of the experiment to the evaluation many steps which may be sources of error (compare chapter 4.2 on page 12). For instance the drying of the catalyst pellets might lasted too long. This appears in the outlines of $M(t)/M_\infty$ where the trend of the curve seems not to subtend the origin as it is pointed up exemplary in figure 11 on the following page.

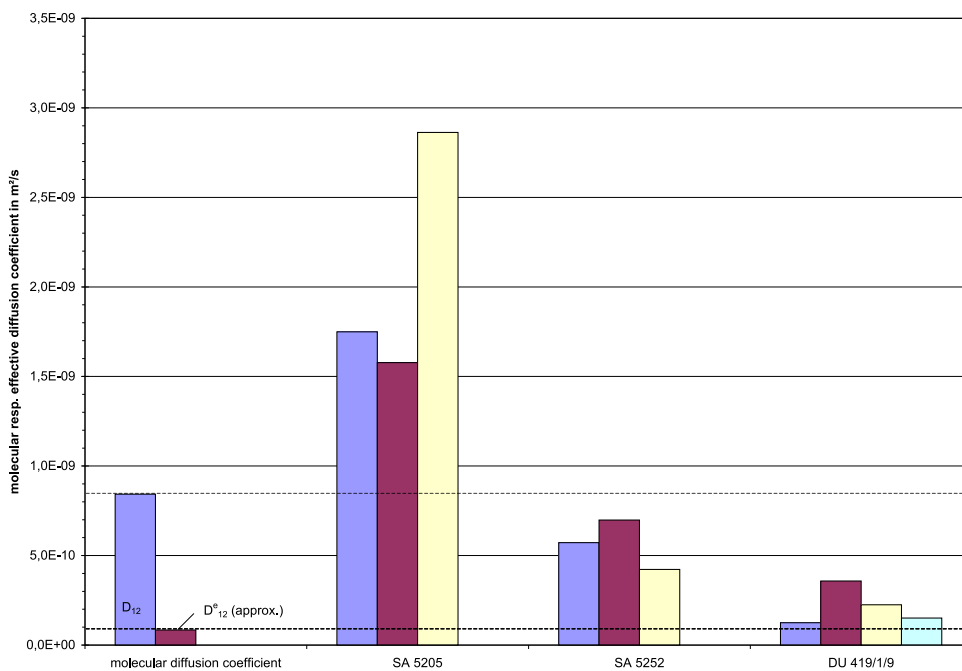


Figure 10: Comparison of effective diffusion coefficients

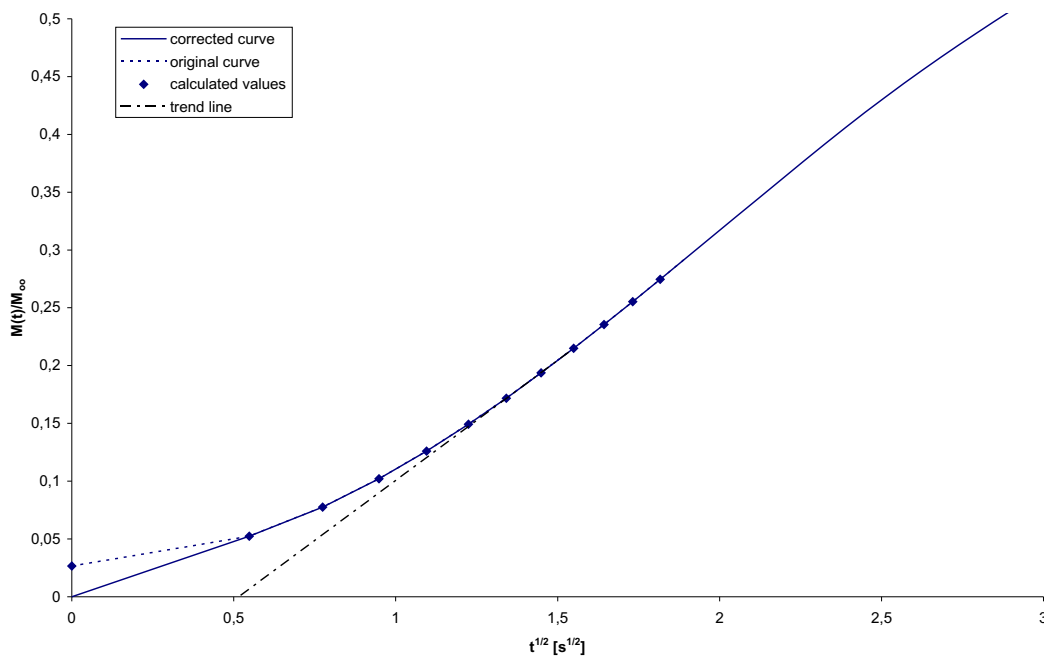


Figure 11: Close-up of the $M(t)/M_{\infty}$ -plot of catalyst SA 5205

Due to corrective procedure carried out in chapter 3.3 the curve however subtends the origin. In order to decrease the effective diffusion coefficient it is necessary to have a small slope in $t = 0$.

However the correction of setting the first value manually to 0 increases the slope. Thus the effective diffusion coefficient would be lower if we use the original slope for the determination. Otherwise an initial value $\neq 0$ doesn't make sense in mathematical perception.

The results of catalysts SA 5252 and DU 460/1/9 match the expected values in a better way. Nevertheless they seem still to be too high in comparison to the approximated effective diffusion coefficient. In this regard the catalyst DU 460/1/9 gives the best result. Concerning the specific data of the catalyst type SA 5252 shows a higher porosity and a higher inner surface than type SA 5205. Type SA 5252 shows the lower diffusion coefficient what might be a sign for a more distinctive fine structure with smaller pores. Concerning the mean pellet diameter no correlation can be found.

As a consequence of unsteady effective diffusion coefficients the values for tortuosity show related results. The sources of error are the same as for determination of molecular and effective diffusion coefficient due to their relation in equation (22). The values for tortuosity are plotted together with the typical range according to [1, page 3] in the figure 12. Mostly the values are far beyond

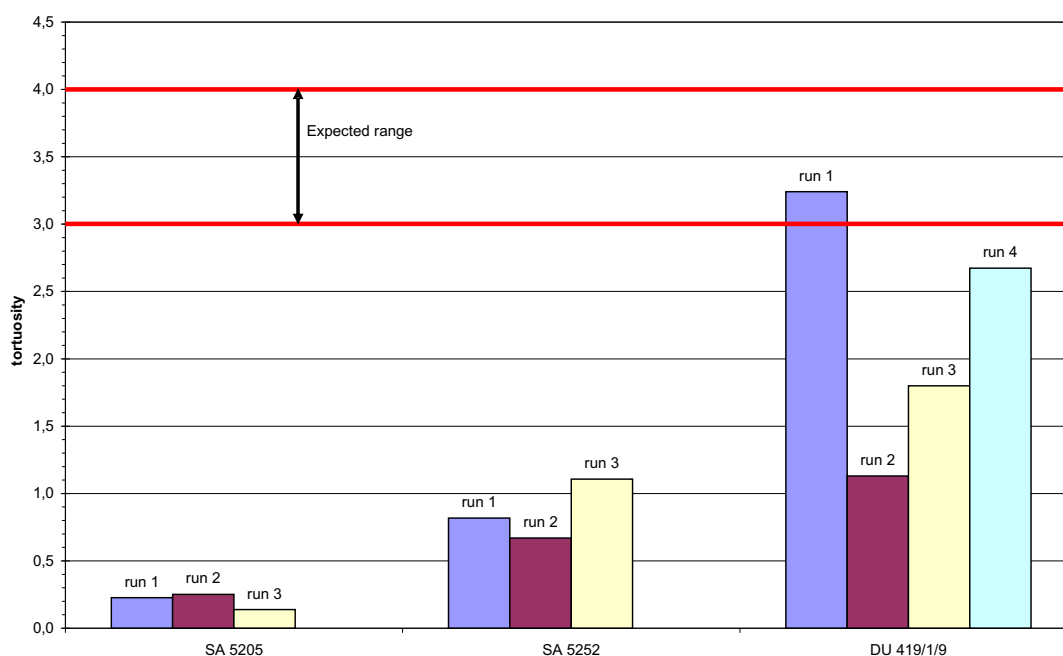


Figure 12: Comparison of tortuosity

the expected range of 3 to 4. Once again the catalyst with the best values for the effective diffusion coefficient type DU 460/1/9 provides the best result for tortuosity: While three out of four values lie beyond the expected range the first test run reaches it.

4.2 Sources of error

- Preparation especially drying of the pellets is not reproducible.
- For the catalysts SA 5252 and DU 460/1/9 the recorder signal doesn't reach the zero line again (compare figures 3 and 4). This influences the results seriously. To avoid this phenomenon the measurement time should be longer.

Appendix

A List of Symbols

Symbol	Description	Unit
c	concentration	$\frac{mol}{m^3}$
c_0	initial concentration	$\frac{mol}{m^3}$
c_i	concentration of component i	$\frac{mol}{m^3}$
d_K	pellet diameter	m
d_M	molecule diameter	m
d_P	pore diameter	m
D_{12}	molecular diffusion coefficient of component 1 within 2	$\frac{m^2}{s}$
D^e	effective diffusion coefficient	$\frac{m^2}{s}$
D_{12}^e	effective diffusion coefficient of component 1 within 2	$\frac{m^2}{s}$
j_1	flux of component 1	$\frac{mol}{m^2 s}$
$M(t)$	amount of substance extracted by diffusion until time t	mol
M_∞	total amount of substance in the pellet an time $t = 0$	mol
n	summation variable	—
r	radius	m
t	time	s
t^*	intersection of the $M/M_\infty = 1$ line	s
z	z-axis coordinate (length)	m
ε	porosity	—
τ	tortuosity	—

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D References

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