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A 46

Internal Friction of gases
(viscosity of gases)

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Objective

From measurements of the viscosity of H_2, CO_2 at 20° and 70° celsius, the mean free path and the colision cross section of the gas should be determined.

Basics

With the viscosity the toughness of a substance is described. With the kinetic gas theory you get the following equations for a dilut gas:

$\eta = \frac{1}{3} \rho \lambda \bar{c}$; ρ: gas density λ: mean free path $\bar{c}$: mean molecular velocity

$\rho = \frac{pM}{RT}$ $\bar{c} = \left[\frac{8RT}{\pi M}\right]^{1/2}$ $\lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2 \left(\frac{N}{V}\right)}$ η: viscosity

p: pressure M: molecular mass R: universal gas constant
T: absolute temperature $\frac{N}{V}$: number density σ: colision cross section

From these equations and by substituting $\frac{1}{3}$ through $\frac{5\pi}{32}$ you get: $\eta = \frac{5\pi}{16} \sqrt{\frac{M_m R T}{\pi}} \frac{1}{N_A \pi \sigma^2}$; N_A: Avogadro's number

As a result, the ~~average~~ mean free path and the colision cross section can be determined as a measure for the molecular diameter.

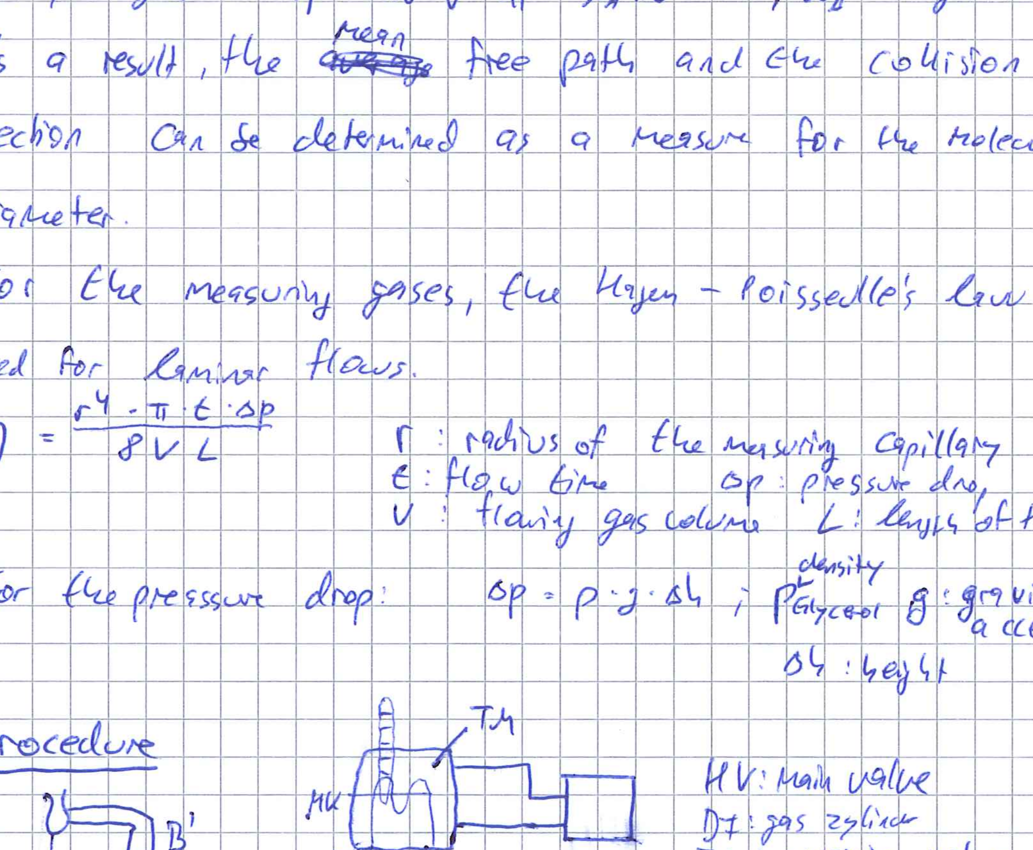
For the measuring gases, the Hagen-Poisseuille's law is used for laminar flows.

$$\eta = \frac{r^4 \cdot \pi \cdot t \cdot \Delta p}{8 V L}$$

r: radius of the measuring capillary
t: flow time Δp: pressure drop
V: flowing gas volume L: length of the capillary

For the pressure drop: $\Delta p = \rho \cdot g \cdot \Delta h$; $\rho_{Glycerol}$: density g: gravitational acceleration
Δh: height

Procedure



HV: main valve
DF: gas zylinder
FV: precision valve
TM: water jacket
MK: measuring capillary
LK: copper cooling coil
S: tube
B & B': markers
A: soap lamella point

A gas cylinder is connected and a pressure of 0,5 to 1 bar is set. Withe the precision valve the height of the glycerol column is set. It should read ~8,5cm.

Lifting and squeezing of the tube S causes gas bubbles from the soap solution. These are carried by the gas through the pipe from B to B'. By measuring the time the bubbles need for this distance, you get the flow time.

But before that the gas has to flow for about 5 min through the apparatus at the respective temperature.

The time is measured 10 times for each gas and each temperature (20°C & 70°C). Also note the pressure difference.

Source: description of experiment A46

data analysis - results

① :

	CO_2		H2		CO2		H2	
	value	±	Value	±	Value	±	value	±
a) T in K	293,5	0,1	294,65	0,1	343,5	0,1	342,65	0,1
V_2 in m^3	3,34E-05	1,62E-08	3,32E-05	1,61E-08	3,34E-05	1,62E-08	3,32E-05	1,61E-08
Δh in m	0,0845	0,002	0,084	0,002	0,0823	0,002	0,086	0,002
b) Δt in s	14,682	0,133	7,666	0,128	18,874	0,282	9,329	0,102
c) Δp in Pa	1044,471	24,721	1038,29	24,721	1017,277	24,721	1063,012	24,721
d) η in kg/m/s	1,54E-05	~~4,09E-06~~ $5{,}12 \cdot 10^{-7}$	8,03E-06	~~2,63E-06~~ $3{,}23 \cdot 10^{-7}$	1,93E-05	~~6,13E-06~~ $7{,}66 \cdot 10^{-7}$	1,00E-05	~~2,77E-06~~ $3{,}46 \cdot 10^{-7}$

calculations:

① a) ideal gas : $pV = nRT \Rightarrow \frac{T_1}{V_1} = \frac{T_2}{V_2}$ with $dp = 0$ $\Rightarrow V_2 = \frac{T_2 \cdot V_1}{T_1}$ with $V_1 = 28{,}5\,cm^3$

$$\Delta V_2 = \left|\frac{\partial V_2}{\partial T_1}\right| \Delta T_1 + \left|\frac{\partial V_2}{\partial T_2}\right| \Delta T_2 = \frac{T_2 V_1}{T_1^2} \Delta T_1 + \frac{V_1}{T_1} \Delta T_2$$ with $\Delta T_1 = 0{,}1\,K$ and $\Delta T_2 = 0{,}05\,K$

b) Δt is the average of our measured times

the error of $\Delta t = \Delta(\Delta t) = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (t_i - \Delta t)^2}$ with $N = 10$

c) from description of experiment : $\Delta p = \rho \cdot g \cdot \Delta h$, with $g = 9{,}81\,\frac{m}{s^2}$, $\rho = (\text{density glycerol}) = 1260\,\frac{kg}{m^3}$

error of $\Delta h = \Delta(\Delta h) = 0{,}002\,m$ because we had to measure the difference and so the error is $\pm 2 \cdot 0{,}001\,m$

$\Rightarrow$ error of $\Delta p = \Delta(\Delta p) = \left|\frac{\partial \Delta p}{\partial \Delta h}\right| \Delta(\Delta h) = |\rho \cdot g| \cdot \Delta(\Delta h)$

d) viscosity $\eta = \frac{r^4 \cdot \pi \cdot t \Delta p}{8 V L}$ from description of experiment

with $r = 0{,}0004\,m = \frac{0{,}0008\,m}{2}$, $L = 30\,cm$, $V = V_2$, $t = \Delta t$ from table

$$\Delta \eta = \left|\frac{\partial \eta}{\partial \Delta t}\right| \Delta(\Delta t) + \left|\frac{\partial \eta}{\partial \Delta p}\right| \Delta(\Delta p) + \left|\frac{\partial \eta}{\partial V_2}\right| \Delta V_2 = \frac{r^4 \pi}{8L} \cdot \left(\frac{\Delta p}{V_2} \Delta(\Delta t) + \frac{\Delta t}{V_2} \Delta(\Delta p) + \frac{\Delta t \Delta p}{V_2^2} \Delta V_2\right)$$

② showing that the viscosity is propotional to $\sqrt{T}$ ($\eta \sim \sqrt{T}$)

$\Rightarrow \eta = c \cdot \sqrt{T} \Leftrightarrow c = \eta \cdot \frac{1}{\sqrt{T}}$

CO_2 : $c_1 = \frac{\eta}{\sqrt{293{,}5\,K}} = 8{,}99 \cdot 10^{-7}\,\frac{kg}{ms\sqrt{K}}$, $c_2 = \frac{\eta}{\sqrt{343{,}5\,K}} = 1{,}04 \cdot 10^{-6}\,\frac{kg}{ms\sqrt{K}}$

H_2 : $c_1 = \frac{\eta}{\sqrt{294{,}65\,K}} = 4{,}68 \cdot 10^{-7}\,\frac{kg}{ms\sqrt{K}}$, $c_2 = \frac{\eta}{\sqrt{342{,}65\,K}} = 5{,}4 \cdot 10^{-7}\,\frac{kg}{ms\sqrt{K}}$

The difference between c_1 and c_2 is in both cases very small (<13,5%), so the relation $\eta \sim \sqrt{T}$ can be asumed. More values to calculate with would give us a more accurate assumption

③ collision cross section for $T = 20°C$ and $p = 1 bar$ with the given equation from the description of the experiment:

$$\eta = 0{,}988\sqrt{\frac{MRT}{\pi}} \cdot \frac{1}{N_A \pi \sigma^2} \iff \sigma = \sqrt{0{,}998\sqrt{\frac{MRT}{\pi}} \cdot \frac{1}{N_A \pi \eta}}$$

with $N_A = 6{,}022 \cdot 10^{23}\,mol^{-1}$
$R = 8{,}314 \frac{J}{mol\,K}$

$\Rightarrow \sigma_{CO_2} = 4{,}47 \cdot 10^{-10}\,m$, $M_{CO_2} = 44{,}01 \frac{g}{mol}$

$\sigma_{H_2} = 2{,}807 \cdot 10^{-10}\,m$, $M_{H_2} = 2{,}01588 \frac{g}{mol}$

mean free path for $T = 20°C$, $p = 1 bar$

$$\eta = \frac{1}{3}\rho \Lambda \bar{c} \quad , \quad \bar{c} = \sqrt{\frac{8RT}{\pi M}} \quad , \quad \rho = \frac{p \cdot M}{RT} \quad \Rightarrow \Lambda = \frac{3\eta}{\rho \bar{c}} = \frac{3\eta}{p}\sqrt{\frac{\pi RT}{8M}}$$

$\Rightarrow \Lambda_{CO_2} = 6{,}82 \cdot 10^{-8}\,m$, $\Lambda_{H_2} = 1{,}66 \cdot 10^{-7}\,m$

error of σ and Λ:

$$\Delta\sigma = \left|\frac{\partial \sigma}{\partial \eta}\right| \Delta\eta = \left| -\frac{1}{2}\sqrt{0{,}988\sqrt{\frac{MRT}{\pi}}\frac{1}{N_A \pi}}\, \eta^{-\frac{3}{2}} \right| \Delta\eta$$

$\Rightarrow \Delta\sigma_{CO_2} = 7{,}39 \cdot 10^{-12}\,m$, $\Delta\sigma_{H_2} = 5{,}84 \cdot 10^{-12}\,m$

$$\Delta\Lambda = \left|\frac{\partial \Lambda}{\partial \eta}\right| \Delta\eta = \left|\frac{3}{p}\sqrt{\frac{\pi RT}{8M}}\right| \Delta\eta$$

$\Rightarrow \Delta\Lambda_{CO_2} = 2{,}26 \cdot 10^{-9}\,m$, $\Delta\Lambda_{H_2} = 6{,}8 \cdot 10^{-9}\,m$

④ comparison of collision diameter with molecular diameters from van der Waals constant b

	CO_2	H_2
$b^{(1)}$	$0{,}0429 \frac{l}{mol}$	$0{,}0265 \frac{l}{mol}$
r_w	$2{,}34 \cdot 10^{-9}\,m$	$1{,}99 \cdot 10^{-9}\,m$
σ	$4{,}47 \cdot 10^{-10}\,m$	$2{,}87 \cdot 10^{-10}\,m$

$b = \frac{RT_c}{8p_c}$ $\quad nRT = (p + \frac{n^2 a}{V^2})(V - nb)$

$\Rightarrow b = N_A \cdot 4\frac{4}{3}\pi r_w^3$

(1): source: CRC-Handbook of Chemistry and Physics, 89th edition, 2009, p. 6-33

$\Rightarrow \sigma$ is much smaller than r_w, but the diffeence is explainable because of the electrostatic Forces, which were left out in ~~de~~ the VdWalls-eqation and the simplification that atoms are balls.

For H_2 the approximation works better, because there are only 2 electrons.

⑤ diffusion: $J = -D\frac{dN}{dz}$, $D = \frac{1}{3}\lambda\bar{c}$ for gases $\lambda = \frac{k_B T}{\sqrt{2}\pi\sigma^2 p}$ $\Rightarrow \lambda$ inversely proportional to p $\Rightarrow D \sim \frac{1}{p}$

$\Rightarrow$ molecules diffuse slowlyier with higher pressure

$\Rightarrow$ higher $T \Rightarrow$ higher $\bar{c} \Rightarrow$ higher D $\Rightarrow$ molecule diffuse quicker with higher temperature

This behaviour is similar to liquids (diffusion ~ T) but liquids are almost inert to pressure alteration.

viscosity: $\eta = \frac{1}{3}\rho\Lambda\bar{c} = \frac{1}{3}M\lambda\bar{c}[A]$ $\Rightarrow$ viscosity η independent of pressure ✓ because higher p leads to higher concentration but lower λ

$\Rightarrow \eta \sim T$ because $\eta \sim \bar{c}$

for fluids: $\eta \sim \frac{1}{T}$, $\eta \sim \frac{1}{p}$ because of the forces between the molecules which are more ~~but~~ bound together than gases.

For liquid, $\eta \sim p$. ~~But~~ If p is changed very small, η is independent.

A46 | Kapillare innen ⌀ 0,8mm
L = 30cm

no O_2

(H_2 : 0,5bar) CO_2 : 0,6bar

20°C

45 start, später 42

Δp = 46, h = 8,5cm
l~8,4

Δh = 0,5cm

t = 20°C

Δt = 0,5s

T_{water} = 14°C

CO_2

bubble	time in s	
(1	15,26)	
2	14,65	8,5
3	14,42	"
4	14,70	"
5	14,78	"
6	14,52	"
7	14,74	"
8	14,71	"
9	14,68	"
10	14,90	"
11	14,72	8,4

H_2 0,3 bar gasflasche
(P = 39 $\frac{ml}{min}$)
T = 21,5°C T_{bath} = 14°C

Δp = 8,3cm

bubbles	time in s	Δp	
1	7,81	[illegible]	[illegible]
2	7,72	[illegible]	8,5
3	7,73	[illegible]	
4	7,77	[illegible]	"
5	7,74		"
6	7,64		"
7	7,64		"
8	7,37		"
9	7,69		"
10	7,55		8,5

70°C

(70,5°C)

ΔT = 1°C

T_{H_2O} = 14,5°C

H_2

bubble	Δt in s	Δp in cm	T in °C
1	9,32	8,6	71
2	9,29	8,6	71
3	9,5	8,6	70,5
4	9,24	8,6	70,5
5	9,43	8,6	70,5
6	9,19	"	70
7	9,23	"	"
8	9,29	"	"
9	9,44	"	"
10	9,36	"	"

CO_2

bubble	Δt in s	Δp in cm	T in °C
1	18,63	8,2	69,5
2	18,83	"	"
3	18,59	8,3	"
4	18,47	"	"
5	18,88	"	"
6	19,06	"	"
7	19,14	"	"
8	19,26	8,2	"
9	18,21	8,1	"
10	18,67	8,1	"

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