Determination of the diffusion coefficient of water vapor and alcohol in air

1 Introduction

Diffusion is the phenomenon of the penetration of two substances into each other, while they are in contact. In this practical, the diffusion coefficient of water vapor and alcohol in the air is determined by evaporation of a drop of water and alcohol, under the condition of stationary diffusion.

The mass of vapor *dm* diffused through the area *dS* over time *dt* is determined by the Fick equation:

$$dm = -D\frac{\partial \rho}{\partial r}dS\,dt, \qquad (1)$$

where $\frac{\partial \rho}{\partial r}$ is the density gradient of water vapor, *D* is the diffusion coefficient.

A drop on a non-wetting substrate takes an oblate shape in the field of gravity, which for simplicity will be considered hemispherical. Under stationary conditions, the mass flow through a hemisphere of arbitrary radius *r* is constant and equal to

$$\frac{dm}{dt} = -2\pi r^2 D\frac{\partial \rho}{\partial r} = const. \qquad (2)$$

The equation 2 gives that

$$r^2\frac{\partial \rho}{\partial r} = C_1 = const. \qquad (3)$$

From equation (3), one can derive the vapor density gradient:

$$\frac{\partial \rho}{\partial r} = \frac{C_1}{r^2}. \qquad (4)$$

Substituting (4) into the diffusion equation (1), one gets:

$$dm = -D\frac{C_1}{r^2}dS\,dt. \qquad (5)$$

To determine the constant C_1, one can write the law of change of the vapor density as the function of distance *r,* integrating (4):

$$\rho(r) = \int\frac{C_1}{r^2}dr + C_2 = -\frac{C_1}{r} + C_2. \qquad (6)$$

The constant C_2 is found from the boundary conditions of the problem. Inside a drop, the density of water does not change with a change in *r*. At distances *r* >> *R*, where *R* is the drop radius, the vapor density decreases according to the equation (6), moreover $r\to\infty\, \rho \to f\rho_{s.v.}$, where *f* is the relative humidity of the air, $\rho_{s.v.}$ is the density of saturated vapors. Which means $C_2 = f\rho_{s.v.}$. At the same time, when *r* = *R*, the vapor density $\rho = \rho_{s.v.}$. Hence, $C_1 = -\rho_{s.v.}(1-f)R$ and as a result:

$$\rho = \rho_{s.v.}(1-f)\frac{R}{r} + f\rho_{s.v.}; \qquad \frac{\partial \rho}{\partial r} = -\frac{\rho_{s.v.}(1-f)R}{r^2}. \qquad (7)$$

Substituting this value of the density gradient into (1), one will get:

$$dm = D\frac{\rho_{s.v.}(1-f)R}{r^2}dS\,dt$$

If the conditions of the experiment are stationary, then the mass of vapors that diffuse over time dt through a hemispherical surface with radius r is equal to:

$$dm=2D\pi r^2\frac{\rho_{s.v.}(1-f)R}{r^2}dt=2D\pi\rho_{s.v.}(1-f)R\,dt. \qquad (9)$$

At the same time, as the hemispherical drop radius decreases from R to $(R\text{-}dR)$, the change in its mass dm_d will be equal to:

$$dm_d=2\pi R^2\rho_l\,dR, \qquad (10)$$

where ρ_l is the density of the liquid.

Taking into account that the decrease in the drop mass is equal to the mass of the diffused vapor: $dm_d=-dm$, using equations (9) and (10), one can associate the diffusion coefficient D with the rate of change of the drop radius R as follows:

$$D=-\frac{\rho_l}{\rho_{s.v.}(1-f)}R\frac{dR}{dt}. \qquad (11)$$

In this work, one will measure the mass of the evaporating hemispherical drop depending on time, instead of its radius. Derive the radius R drops through its mass m_d: $R=\left(\frac{3m_d}{2\pi\rho_l}\right)^{1/3}$. The derivative $\frac{dR}{dt}$ can be connected with the derivative $\frac{dm_d}{dt}$. As can be seen from (10), $\frac{dm_d}{dt}=2\pi R^2\rho_l\frac{dR}{dt}$, or $\frac{dR}{dt}=\frac{1}{2\pi R^2\rho_l}\frac{dm_d}{dt}$. After substituting this derivative into formula (11), it can be rewritten as follows:

$$D=-\frac{1}{2\pi\rho_{s.v.}(1-f)}\left(\frac{2\pi\rho_l}{3m_d}\right)^{1/3}\frac{dm_d}{dt}.$$

Taking into account $(m_d^{1/3})\frac{dm_d}{dt}=\frac{3}{2}\frac{d(m_d^{2/3})}{dt}$, one will get:

$$D=-\frac{3}{2}\frac{1}{2\pi\rho_{s.v.}(1-f)}\left(\frac{2\pi\rho_l}{3}\right)^{1/3}\frac{d(m_d^{1/3})}{dt},$$

or

$$D=\frac{1}{2\rho_{s.v.}(1-f)}\left(\frac{9\rho_l}{4\pi^2}\right)^{1/3}\left|\frac{d(m_d^{2/3})}{dt}\right|. \qquad (12)$$

From the obtained expression it is clear that for the experimental determination of D it is necessary to measure the change in the mass of the drop over time under stationary conditions.

2 Experimental setup

The experimental setup consists of a digital balance, which measures the mass of the drop with a precision of *0.1* mg, and a fluoroplastic substrate, onto which a drop of the test liquid is squeezed out. When a drop evaporates, the balance readings change continuously. The time is measured with a stopwatch. Air temperature and its relative humidity are measured using a hygrometer.

3 Measurement and data processing

Switch on the digital balance and leave it to warm up for 10 minutes.

Task 1. Measurement of the mass of an evaporating drop of water

Put a fluoroplastic substrate on the balance. After waiting a few seconds, press the "Zero / Tare" button. Wait until the balance is reset. Use a syringe with water, to squeeze gently a drop of water in the middle of the substrate (take a try before you start the measurements and squeeze a few drops on a sheet of paper). The initial mass of the drop should be from *2 - 4* mg (if the mass is too large, the drop will evaporate too long). Close the doors of the balance. Watch the balance reading. After a few seconds, it stabilizes. When the weight of the drop decreases by *0.1* mg (the unit of the last digit of the balance reading), start the stopwatch. Record the each points in time when the weight will decrease by *0.1* mg. Put down into the table the values of the mass m of the evaporating drop and the corresponding values of time t. Continue the measurements until the mass of the drop reaches the values of *0.5 - 0.3* mg. The measurements take from 20 up to 30 minutes, depending on the initial mass of the drop.

Task 2. Measurement of the mass of an evaporating drop of alcohol

Repeat the measurements described in task 1 with a drop of alcohol. Note that alcohol evaporates much faster, so the initial mass of the drop may be greater. It is necessary to monitor the reading of the balance carefully, managing to record the time. Repeat this measurement with 3 different drops of alcohol (each measurement will take about three minutes).

Task 3. Calculation of diffusion coefficients of water and alcohol molecules in the air

For each measurement, plot a graph of $m_d^{2/3}$ vs time. Using the graph, determine the derivative $\frac{d(m_d^{2/3})}{dt}$ and calculate the diffusion coefficient in accordance with the formula (12). The value of the density of saturated water vapor at the ambient temperature, can be determined from the table 1 (table 1 can be found in the appendix to this practical), the relative humidity f of the air determined with a hygrometer, in the laboratory.

While calculating D of alcohol in accordance with formula (12), note that for this case $f = 0$. Density of saturated vapors of ethanol C_2H_5OH $\rho_{s.v.}$ = 110 g/m^3 at ambient temperature of *17 – 22* ºC.

Task 4. Estimation of the mean free path of water and alcohol molecules in the air

Calculate the average velocity of molecules of water and alcohol according to the formula $\overline{v}=\sqrt{\frac{8}{\pi}\frac{RT}{M}}$, where R is the molar gas constant, M is the molar mass. From the formula $D=\frac{1}{3}\overline{v}\lambda$, one can find the mean free path of water vapor and alcohol molecules in the air.

4 Questions

1. The mean free path of molecules depends on the gas concentration n and the scattering cross section $\sigma = \pi d^2$ (d is the effective diameter of molecules): $\lambda = \frac{1}{\sqrt{2} n \sigma}$. How should one modify the mean free path formula to estimate the mean free path of water or alcohol molecules in the air.

2. How does the mean free path of molecules depend on pressure and temperature? At what pressure does the mean free path of air molecules equal *1* mm, if at atmospheric pressure it is equal to 6×10^{-6} cm?

3. Does the mean free path of molecules change when the gas is heated in a closed vessel?

4. Based on the differential equation (11), calculate how much time is needed for the drop radius to decrease by a factor of 2.

5. Using dimensional considerations, determine the dependence of the average diffusion displacement of particles on time.

6. If the smell of a substance spreads by diffusion over a distance of *1* m during time t_1, then in what time t_2 will it spread to *10* meters?

Appendix

Table 1. The density of saturated vapor of water $\rho_{s.v.}$ at various ambient temperatures t °C.

t, °C	$\rho_{s.v.}$, g/m^3	t, °C	$\rho_{s.v.}$, g/m^3	t, °C	$\rho_{s.v.}$, g/m^3
13	11,4	17	14,5	21	18,3
14	12,1	18	15,4	22	19,4
15	12,8	19	16,3	23	20,6
16	13,6	20	17,3	24	21,8

Table 2. The diffusion coefficient D at atmospheric pressure

Diffusive component	Main component	t, °C	D, m^2/s
Water vapor	Air	0	$0{,}23 \times 10^{-4}$
Ethanol vapor	Air	0	$0{,}10 \times 10^{-4}$

Table 3. $k^{2/3}$ as the function of k = 5.0 … 0.3

k	$k^{2/3}$	k	$k^{2/3}$	k	$k^{2/3}$	k	$k^{2/3}$	k	$k^{2/3}$	k	$k^{2/3}$
5,0	2,92	4,2	2,60	3,4	2,26	2,6	1,89	1,8	1,48	1,0	1,0
4,9	2,88	4,1	2,56	3,3	2,22	2,5	1,84	1,7	1,42	0,9	0,93
4,8	2,85	4,0	2,52	3,2	2,17	2,4	1,79	1,6	1,37	0,8	0,86
4,7	2,81	3,9	2,48	3,1	2,13	2,3	1,74	1,5	1,31	0,7	0,79
4,6	2,77	3,8	2,44	3,0	2,08	2,2	1,69	1,4	1,25	0,6	0,71
4,5	2,73	3,7	2,39	2,9	2,03	2,1	1,64	1,3	1,19	0,5	0,63
4,4	2,69	3,6	2,35	2,8	1,99	2,0	1,59	1,2	1,13	0,4	0,54
4,3	2,64	3,5	2,31	2,7	1,94	1,9	1,53	1,1	1,07	0,3	0,45