Workshop 8: Evaporation and stagnant-gas diffusion

Attempt these problems before opening the worked solutions.

1 Methanol emission from an open tank

EXERCISE

Exercise 1. Planar diffusion through stagnant air

A tank (diameter = 1m, height = 3 m) containing liquid methanol (MW = 32 g/mol) has its top open to the atmosphere. The level of methanol in the tank is maintained at 0.5 m. The gas space inside the tank is stagnant and the methanol vapours are immediately dispersed once they exit the tank. Engineers on-site are concerned that this open tank may be emitting a considerable amount of methanol vapour.

a. What is the emission rate of methanol vapour from the tank (in $\mathrm{kg\ methanol/day}$) when the temperature of the tank is $30\,^{\circ}\mathrm{C}$? State all assumptions and boundary conditions.

b. If the temperature of the tank is raised to $40\,^{\circ}\mathrm{C}$, what is the new emission rate?

Data: Vapour pressure of MeOH = 163 mmHg ($30\,^{\circ}\mathrm{C}$); 265 mmHg ($40\,^{\circ}\mathrm{C}$)

D_{AB} (methanol/air) @ 298 K = $0.162 \times 10^{-4}\ \mathrm{m^2/s}$.

See solution for Exercise 1

2 Evaporation of a suspended water droplet

EXERCISE

Exercise 2. Spherical diffusion and a shrinking liquid balance

Consider the evaporation of water droplets (diameter ~ 0.1 mm) in still air at $50\,^{\circ}\mathrm{C}$, 1 atm pressure, with 20% relative humidity. As the droplets are very small, it can be considered that their terminal velocity is negligible, i.e. they are suspended in air. The droplet temperature can be assumed to be at $50\,^{\circ}\mathrm{C}$ and its vapour pressure is 12 kPa. If the diffusion coefficient of water vapour in air is $0.288\ \mathrm{cm^2/s}$,

a. Calculate the initial rate of evaporation of a single droplet, assuming steady state condition.

b. Determine the time required for the water droplet to evaporate completely.

See solution for Exercise 2

Solutions

Exercise solutions

Exercise 1. Planar diffusion through stagnant air

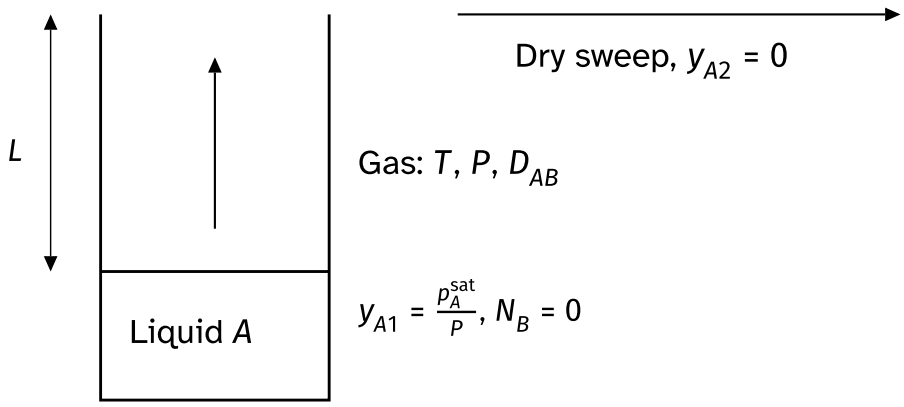


Figure 1: The open tank has the same one-dimensional gas-space model as this evaporation tube. The diffusion distance is the tank height minus the maintained liquid depth.

Data

Quantity	Symbol	Value
Tank diameter	d	$1.0\ \mathrm{m}$
Gas depth above maintained liquid level	L	$3.0 - 0.5 = 2.50\ \mathrm{m}$
Atmospheric pressure	P	$101325\ \mathrm{Pa} = 760\ \mathrm{mmHg}$
Methanol molar mass	M_A	$0.032\ \mathrm{kg\ mol^{-1}}$
Reference diffusivity	$D_{AB}(298)$	$1.62 \times 10^{-5}\ \mathrm{m^2\ s^{-1}}$
Saturation pressure at 30 and 40 degrees Celsius	p_{sat}	$163,265\ \mathrm{mmHg}$

We need the total daily emission from the open tank at each temperature.

Assumptions

- Steady one-dimensional diffusion through the gas space.
- Uniform temperature in each calculation and ideal-gas behaviour.
- Constant pressure, maintained liquid level and saturated vapour at the surface.
- Zero net air flux through the liquid; dry gas at the tank mouth.
- Natural convection, wind penetration and transport through the walls are neglected.

Calculations

Let A denote methanol and B denote air. Coordinate s points upwards from the liquid. Zero net air flux permits Stefan flow of the mixture, so use

$$N_A = -\frac{cD_{AB}}{1-y_A}\frac{dy_A}{ds}, \qquad c = \frac{P}{RT} \tag{1}$$

Here $R = 8.314\,\mathrm{Pa\,m^3\,mol^{-1}\,K^{-1}}$. The boundary values are $y_A(0) = p_{sat}/P$ and $y_A(L) = 0$. At the same pressure, estimate the change in diffusivity from

$$D_{AB}(T) = D_{AB}(298)\left(\frac{T}{298}\right)^{3/2}$$

Integrate Eq. 1 across the gas space and multiply the flux by the open cross-sectional area, molar mass and seconds per day.

The maintained liquid level fixes the gas diffusion distance throughout each calculation.

Since N_A is constant over the planar gas space, integration gives

$$N_A = \frac{cD_{AB}}{L}\ln\frac{1-y_A(L)}{1-y_A(0)}. \tag{2}$$

At 30 degrees, $T = 303.15\,\mathrm{K}$,

$$y_A(0) = \frac{163}{760} = 0.214474,$$

$c = 40.2021\,\mathrm{mol\,m^{-3}}$ and $D_{AB} = 1.66218 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$.

Using Eq. 2 gives $N_A = 6.45246 \times 10^{-5}\,\mathrm{mol\,m^{-2}\,s^{-1}}$.

The emitting area is

$$A = \frac{\pi(1.0)^2}{4} = 0.785398\,\mathrm{m^2},$$

hence

$$\dot{m}_A = M_A A N_A = 1.62168 \times 10^{-6}\,\mathrm{kg\,s^{-1}},$$

$$m_{A,day} = 86400\dot{m}_A = 0.1401\,\mathrm{kg\,day^{-1}}.$$

At 40 degrees, $T = 313.15\,\mathrm{K}$, $y_A(0) = 0.348684$, $c = 38.9183\,\mathrm{mol\,m^{-3}}$ and $D_{AB} = 1.74510 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$.

The same integration yields

$$N_A = 1.16479 \times 10^{-4}\,\mathrm{mol\,m^{-2}\,s^{-1}} \qquad m_{A,day} = 0.2529\,\mathrm{kg\,day^{-1}}$$

The predicted emission increases by a factor of 1.805.

Increased saturation vapour pressure is the main cause, with a smaller diffusivity increase and a slight gas-concentration decrease.

These rates require the assumed stagnant gas space; ventilation or buoyant circulation would change the model.

Answer

The methanol emission is $0.140\,\mathrm{kg\,day^{-1}}$ at $30\,^{\circ}\mathrm{C}$ and $0.253\,\mathrm{kg\,day^{-1}}$ at $40\,^{\circ}\mathrm{C}$, under the stagnant-gas model.

Back to Exercise 1

Exercise 2. Spherical diffusion and a shrinking liquid balance

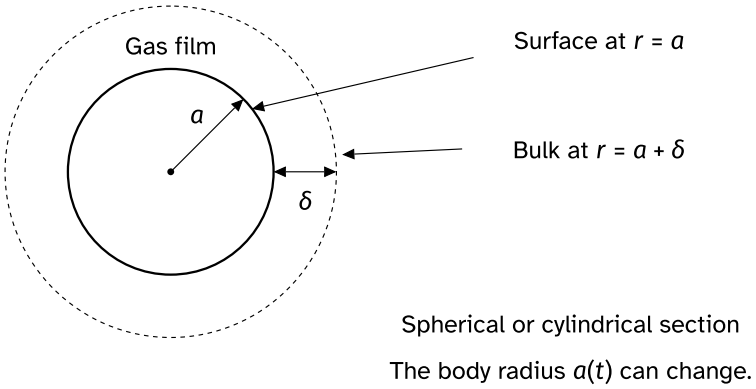


Figure 2: The droplet evaporates into air with a fixed far-field humidity. Its surface concentration is saturated, while its radius decreases as liquid is lost. The dashed outer boundary is taken to infinity in this problem.

Data

Property	Value
Total pressure P	$101325\,\mathrm{Pa}$
Temperature T	$323.15\,\mathrm{K}$
Water saturation vapour pressure p_{sat}	$12000\,\mathrm{Pa}$
Water-air diffusivity D_{AB}	$0.288\,\mathrm{cm^2\,s^{-1}}$
Liquid water density ρ_L	$1000\,\mathrm{kg\,m^{-3}}$
Water molar mass M_A	$0.018\,\mathrm{kg\,mol^{-1}}$

Assumptions

Assume spherical symmetry, negligible droplet velocity, constant properties and no air dissolving in the droplet. The gas profile adjusts much faster than the droplet shrinks, so treat it as steady at each instantaneous radius $a(t)$. An external heat supply maintains the liquid and gas at 50 degrees; ignore evaporative cooling. Far-field humidity stays fixed in an effectively

infinite gas domain. At $r = a$, $y_s = p_{sat}/P$. At $r \to \infty$, $y_\infty = 0.20 p_{sat}/P$. Relative humidity is a ratio of water partial pressure to saturation pressure, not a gas mole fraction.

Calculations

Derive $r^2 N_A = \text{constant}$ from a spherical gas shell balance. Integrate Eq. 1 radially using $N_B = 0$. Then use the shrinking liquid balance

$$-\rho_L 4\pi a^2 \frac{da}{dt} = M_A \dot{n}_A,$$

where $\dot{n}_A = 4\pi r^2 N_A$ is the molar evaporation rate. Use the instantaneous rate as the radius decreases; do not divide the initial mass by the initial rate to obtain the lifetime.

The spherical area increases outward while the total molar evaporation rate stays constant.

A steady shell balance gives

$$\frac{d(r^2 N_A)}{dr} = 0.$$

Write $r^2 N_A = C$ and integrate the flux law between a and infinity:

$$\begin{aligned} \frac{C}{a} &= c D_{AB} \Lambda, \\ \Lambda &= \ln \frac{1 - y_\infty}{1 - y_s}, \\ \dot{n}_A &= 4\pi a c D_{AB} \Lambda. \end{aligned} \tag{3}$$

Convert $D_{AB} = 2.88 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$ and

$$a_0 = \frac{d_0}{2} = 5.00 \times 10^{-5}\,\mathrm{m}.$$

The boundary fractions are $y_s = 0.118431$ and $y_\infty = 0.0236862$, so $\Lambda = 0.102081$ and $c = 37.7140\,\mathrm{mol\,m^{-3}}$.

Using the initial radius in Eq. 3 gives

$$\dot{n}_A(0) = 4\pi(5.00 \times 10^{-5})(37.7140)(2.88 \times 10^{-5})(0.102081)$$

Evaluating the initial rate gives

$$\dot{n}_A(0) = 6.96655 \times 10^{-8}\,\mathrm{mol\,s^{-1}},$$

$$\dot{m}_A(0) = M_A \dot{n}_A(0) = 1.2540 \times 10^{-9}\,\mathrm{kg\,s^{-1}}.$$

Substitute the instantaneous rate into the liquid balance, cancel $4\pi a$ and integrate:

$$
\begin{aligned}
-\rho_L a \frac{da}{dt} &= M_A c D_{AB} \Lambda, \\
a^2(t) &= a_0^2 - \frac{2 M_A c D_{AB} \Lambda}{\rho_L} t, \\
t_f &= \frac{\rho_L a_0^2}{2 M_A c D_{AB} \Lambda} \\
&= 0.6263\,\mathrm{s}.
\end{aligned}
$$

The initial liquid mass is $5.2360 \times 10^{-10}\,\mathrm{kg}$.

Dividing it by the initial mass rate gives 0.4175 s and underestimates the lifetime because the rate decreases with radius.

The gas diffusion time

$$
\frac{a_0^2}{D_{AB}} = 8.68 \times 10^{-5}\,\mathrm{s}
$$

is much shorter than t_f, which supports the quasi-steady approximation.

Complete evaporation is the $a \to 0$ limit of this continuum model.

Cooling and molecular-scale effects are outside the assumptions.

Answer

The initial mass evaporation rate is $1.25 \times 10^{-9}\,\mathrm{kg\,s^{-1}}$ per droplet. The shrinking-sphere model gives a lifetime of $0.626\,\mathrm{s}$, with the droplet temperature maintained at $50\,^{\circ}\mathrm{C}$.

Back to Exercise 2