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1 Chem 30324, Spring 2018, Homework 2 Solution

1.1 Problem 1. Gases on a table top

1.1.1 Derive the Maxwell-Boltzmann speed distribution for a 2-dimensional gas.

The Maxwell-Boltzmann distribution for 2 dimensions can be derived by considering each dimension as independent.
In cartesian coordinates, the distribution looks like

$$P(v)dv_xdv_y = \frac{m}{2\pi k_B T} e^{\frac{-m(v_x^2 + v_y^2)}{2k_B T}}$$

When converted to polar coordinates, the distribution is

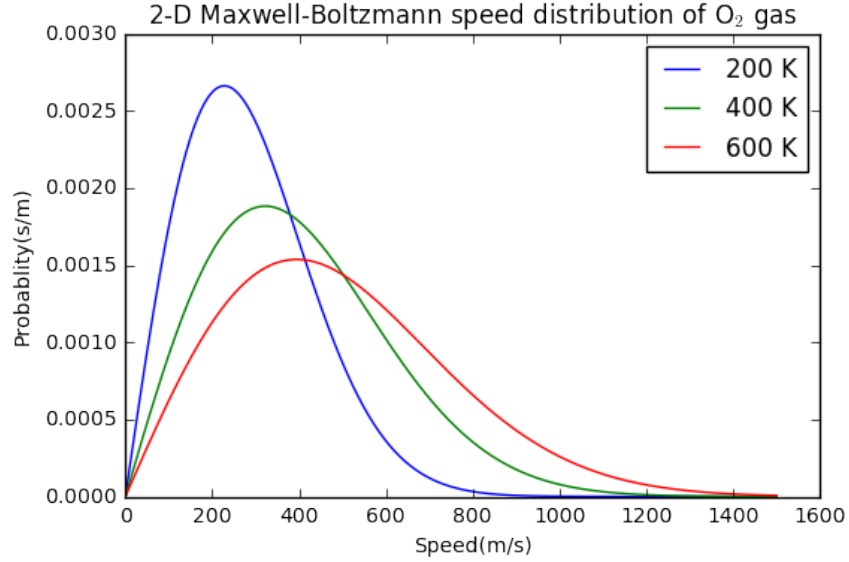
$$P(v)dv = \int_0^{2\pi} \frac{m}{2\pi k_B T} e^{\frac{-mv^2}{2k_B T}} v dv d\theta$$

which finally gives:

$$P(v)dv = \frac{mv}{k_B T} e^{\frac{-mv^2}{2k_B T}} dv$$

1.1.2 Plot this 2-dimensional speed distribution for O₂ molecules at 200, 400 and 600 K.

The speed distribution looks like:



1.1.3 Calculate the mean (expected value) of the speed of a 2-dimensional gas of molecules. How does your answer compare to a 2-dimensional gas?

The mean value of speed can be calculated through:

$$\langle v \rangle = \int_0^{\infty} v P(v) dv$$

The mean value comes out to be :

$$\langle v \rangle = \sqrt{\frac{\pi k_B T}{2m}}$$

This value is different from that of a 3-dimensional gas where

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

Both results are dependent on $(T/m)^{0.5}$

1.1.4 Calculate the mean kinetic energy of a 2-dimensional gas. How does your answer compare to a one and 3-dimensional gas?

The mean value of kinetic energy can be calculated through:

$$\langle K \rangle = \int_0^{\infty} \frac{mv^2}{2} P(v) dv$$

The mean value comes out to be $k_B T$

Mean value of 1-D gas : $0.5k_B T$

Mean value of 3-D gas : $1.5k_B T$

They are all multiples of $0.5k_B T$ since the velocity components in different directions are assumed independent of each other.

1.2 Problem 2. (Kinetics and Transport)

1.2.1 What does gas kinetic theory predict for the gas self-diffusion constant D_{11} of CO_2 gas in the cell, in cm^2/s ?

Taking $m = 44 \cdot m_p = 44 \cdot 1.6605 \cdot 10^{-27} = 73.062 \cdot 10^{-27}$

$k = 1.38 \cdot 10^{-23} \text{ J/K}$

$T = 298 \text{ K}$

$d = 0.4 \cdot 10^{-9} \text{ m}$

$p = 10^5 \text{ Pa}$

The mean speed is calculated as :

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} = 378.592 \text{ m/s}$$

Collision cross section is given by:

$$A = \pi \cdot d^2 = 5.0265 \cdot 10^{-19} \text{ m}^2$$

Mean free path is given by :

$$l = kT / \sqrt{2} A p = 5.785 \cdot 10^{-8} \text{ m}$$

Self diffusion constant is given by:

$$D_{11} = 1/3 \langle v \rangle l \cdot 10000 = 7.30064 \cdot 10^{-2} \text{ cm}^2/\text{s}$$

1.2.2 Use the Stokes-Einstein relationship to estimate the diffusion constant of CO_2 in the Stoddard solvent. How does this compare with the diffusion constant in the gas phase? Why?

$$r = d/2 = 0.2 \cdot 10^{-9} \text{ m}$$

Viscosity, $\eta = 1 \cdot 10^{-3} \text{ kg/m.s}$

The diffusion constant in Stoddard solvent is:

$$D_2 = kT/(4\pi\eta r) * 10000 = 1.63627 * 10^{-5} \text{ cm}^2/\text{s}$$

It's less than that of the gas phase by 3 orders of magnitude.
That's because mean free path length in liquid phase is less than for the gas phase.

- 1.2.3 We found in class that the probability for a molecule to diffuse a distance x in time t is Gaussian with mean 0 and standard deviation = $2 D_{11} t$. About how long will it take for 1/3 of the molecules starting at the center of the gas space to diffuse all the way to the surface of the liquid, i.e., $> 1 \text{ cm}$?**

To get the time for 1/3 of molecules to diffuse

We use the Gaussian probability distribution for diffusion

$$P(x, t) = \frac{e^{\frac{-x^2}{4D_{11}t}}}{2\sqrt{\pi D_{11}t}}$$

To get the time of 1/3 molecules to diffuse,

we set the integral of distribution from 1 cm to infinity as 1/3:

$$\int_1^{\infty} P(x, t) dx = 1/3$$

After integration, the solution is 36.915 s

(Another way to go about it is given in the python notebook)

- 1.2.4 How many collisions on average does one of these diffusing CO₂ molecule make with other gas molecules on the way from the middle of the vapor space to the surface of the solvent?**

Total distance travelled by molecules in the above time:

= mean speed * time

= $378.592 * 36.915 = 13975.723 \text{ m}$

Number of collisions = Total distance/mean free path

= $2.41582 * 10^{11}$

1.2.5 How far in total distance does this typical CO₂ molecule travel in the time it takes to reach the solvent surface from the middle of the cell?

Total distance = Mean free path*Number of collisions
 = 1.3975×10^4 m

1.2.6 How many CO₂ molecules impinge on the surface of the Stoddard solvent in one second?

Total wall collision frequency J_w is given as:

$$J_w = \frac{N \langle v \rangle}{4V} = \frac{p \langle v \rangle}{4kT} = 2.3015 \times 10^{27} \text{ coll/m}^2 \text{ s}$$

Area of surface = $\pi \cdot 0.02^2 = 1.2566 \times 10^{-3} \text{ m}^2$

Time = 1s

Number of molecules = $J_w \cdot \text{Area} \cdot \text{Time} = 2.8921 \times 10^{24}$

1.2.7 Using your estimate of the diffusion constant in the solvent, how long does it take the same fraction CO₂ molecules to diffuse a similar distance in 1-dimension in the liquid phase?

Taking $D_2 = 1.63627 \times 10^{-5} \text{ cm}^2/\text{s}$ in

$$P(x, t) = \frac{e^{-\frac{x^2}{4Dt}}}{2\sqrt{\pi D_{11} T}}$$

We do the same procedure as before

To get the time of 1/3 molecules to diffuse,

we set the integral of distribution from 1 cm to infinity as 1/3:

$$\int_1^{\infty} P(x, t) dx = 1/3$$

After integration, the solution is 164706.113s

(Another way to go about it is given in the python notebook)

1.2.8 Is it safe to assume that any CO₂ that travels from the surface into the bulk of the solvent is rapidly replaced from the gas phase?

By looking at the answers obtained in part 5 and 6 (or even 7 and

11) It is clear that CO_2 molecules travel faster in gas phase. So it is safe to assume that the diffusing molecules are rapidly replaced.

1.2.9 Suppose the volume of the gas-handling manifold is 100 cm^3 and is pressurized with CO_2 in the morning to 1.1 atm . What will the pressure in the manifold be four hours later, when lab starts, if the manifold has a pinhole of $1 \mu \text{ m}^2$?

$$V = 100 \text{ cm}^3 = 10^{-4} \text{ m}^3$$

$$P_0 = 1.1 \times 101325 = 111457.5 \text{ Pa}$$

$$A = 1 \mu \text{ m}^2 = 10^{-12} \text{ m}^2$$

$$\text{Given time} = 4 \text{ hr} = 14400 \text{ s}$$

Time constant is given by:

$$\tau = \frac{V}{A} \sqrt{\frac{2\pi m}{k_B T}} = 1.0565 \times 10^6 \text{ s}$$

$$\text{Pressure } P = P_0 e^{\frac{-\text{time}}{\tau}} = 109948.71 \text{ Pa} (1.085 \text{ atm})$$