1-2023

Calculating Avogadro's Number

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1 Abstract

The value of Avogadro's number is found by using kinetic theory along with (a) the volume change upon sublimation of a small quantity of dry ice (CO_2), and (b) the diffusion length, as a function of time, of iodine in air at a certain temperature.[1]

2 Introduction

The kinetic theory of matter is considered to be one of the first to explain the structure of matter. In this experiment, you will follow some of its basic assumptions about simple molecules:

1. They behave like hard spheres.
2. Their behavior at different temperatures can be described by a **mean speed**, $\langle v \rangle$. We will use the symbol $\langle\ \rangle$ to represent an average or mean value.
3. They are about the same size. That is, they all have about the same diameter, say d (Fig. 1).
   a. Molecules in liquids and solids are practically incompressible, thus they are closely packed. The average volume allocation per molecule is about d^3(Fig. 1a).
   b. Molecules in gases are compressible, thus they are far of each other. The average volume allocation per molecule is about D^3(Fig. 1b).

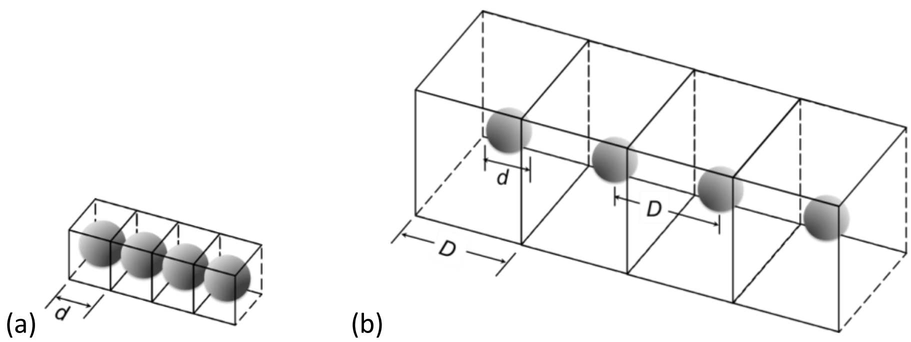

Figure 1 (a) Solid or Liquid state (closely packed) with a volume $\sim d^3$ per molecule. (b) Gaseous state (loose packing) with a volume D^3 per molecule.

When a molecule moves, it will travel an average distance (step) before it collides with another molecule. This displacement in between successive collisions is called the **mean free path** λ. This is related to the average distance a molecule will advance (diffuse) after it takes $N_{\mathrm{collision}}$ collisions. This distance is called the **diffusion length** (S_{rms}) which it is found by solving a random walk problem.

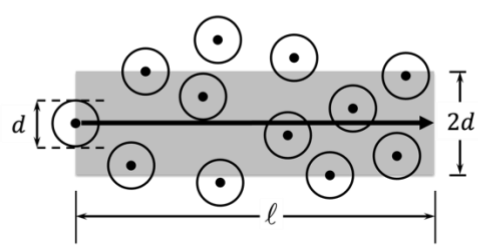

Figure 2. All molecules are frozen momentarily in their random positions, except for the one on the left. The moving molecule travels at a average relative speed with respect to the other ones.

To calculate the mean free path of molecules in their gaseous state, we are going to assume that all molecules are frozen momentarily in their random positions, except for one (Fig. 2). Suppose that the moving molecule travels at a mean relative speed of $\langle v\rangle_{\mathrm{rel}}$ with respect to other molecules (this will be the speed with which one molecule approaches another of the same kind). Using the Maxwell–Boltzmann distribution we can find that $\langle v\rangle_{\mathrm{rel}} = \sqrt{2}\langle v\rangle$, where $\langle v\rangle$ is the mean speed of the molecules in a gas. In a time Δt, the moving molecule will collide with all the molecules whose centers are inside the volume of a cylinder of cross-section σ and length ℓ, ($V = \sigma\ell$, Fig. 2). The number of collisions made by the molecule during this time is called the **collision frequency**, given by $z = N_{\mathrm{C}}/\Delta t$, where N_{C} is the number of collisions.

We can write the collision frequency in terms of the molecular density, $\mathcal{N}$ i.e., the number of molecules per volume in the gas, $\mathcal{N} = N/V$, as

$$z = \sigma\langle v\rangle_{\mathrm{rel}}\mathcal{N} \tag{1}$$

On the other hand, the frequency can also be written as $z = 1/\tau$, where $\tau = \Delta t/N_{\mathrm{C}}$ is the time between two consecutive collisions.

We are now able to find a relationship between the mean free path and the collision frequency Say the molecule is traveling with mean speed $\langle v\rangle$, the distance traveled during two consecutive collisions is given by

$$\lambda = \langle v\rangle\tau = \frac{\langle v\rangle}{z} \tag{2}$$

Using Eq. (1):

$$\lambda = \frac{\langle v\rangle}{\sigma\langle v\rangle_{\mathrm{rel}}\mathcal{N}} = \frac{\langle v\rangle}{\sigma\left(\sqrt{2}\langle v\rangle\right)\mathcal{N}} = \frac{1}{\sqrt{2}\sigma\mathcal{N}}$$

A good approximation is to assume that the cylinder has a diameter $2d$, thus $\sigma = \pi d^2$, and so

$$\lambda = \frac{1}{\sqrt{2}\pi\mathcal{N}d^2} \tag{3}$$

Normally, molecules change their direction of motion after each collision. This is an example of diffusive motion, or **diffusion**, also known as *random walk*. Suppose we run the experiment in Fig. 2, i.e., we allow the molecule to head to the right hoping that it will travel a total distance ℓ. It starts moving forward until it collides with another molecule making it change its direction; then it moves with this new direction until another collision happens, making it change its direction again until a third collision happens, and so on. At a certain time Δt, the molecule has had N_{C} collisions and the same number of random direction changes.

These random direction changes can make the molecule move back to its starting point or be as far away as ℓ. The most likely outcome is that the molecule will be somewhere between 0 and ℓ. If we perform the experiment many times, we can predict the average displacement, $\langle S\rangle$ is in fact proportional to the square root of the time that it has been moving, $\langle S\rangle \propto \sqrt{\Delta t}$. Additionally, it can be proved that $\langle S^2\rangle = N_{\mathrm{C}}\lambda^2$, thus the root-mean-square (rms)value of the average displacement, $S_{\mathrm{rms}} = \sqrt{\langle S^2\rangle}$, is given by

$$S_{\mathrm{rms}} = \lambda\sqrt{N_{\mathrm{C}}} \tag{4}$$

3 Methodology

This experiment has two parts: (1) you are going to measure the volume change upon sublimation of a small quantity of dry ice (CO_2), and (2) you are going to time of diffusion of iodine vapor in air, at a certain temperature $T_{\mathrm{I-tube}}$. Both measurements will allow us to find a value for Avogadro's number.

3.1 Dry ice sublimation

As mentioned before, the center-to-center distance in liquids and solids molecules equals the molecular diameter. Thus, the volume of a solid, V_{solid}, is approximately equal to Nd^3, where N is the number of molecules it contains. Gases on the other hand are compressible. When the dry ice sublimates at room temperature the average center-to-center distance, of the $\mathrm{CO_2}$

molecules, is D, hence N number of molecules will occupy a volume of $V_{\text{gas}} = ND^3$. Both volumes can be measured for a given quantity of dry ice, so their ratio is easily determined to be:

$$\frac{V_{\text{gas}}}{V_{\text{solid}}} = \frac{D^3}{d^3} \tag{5}$$

Since the volume occupied by **one molecule** in the gaseous state is on the average D^3, the molecular density can be written as $\mathcal{N} = 1/D^3$, thus $D^3 = d^3(V_{\text{gas}}/V_{\text{solid}})$. This last result can be used with Eq. (3) to find the average diameter of each molecule, d:

$$\lambda = \frac{1}{\sqrt{2}\,\pi\mathcal{N}d^2} = \frac{1}{\sqrt{2}\,\pi}\frac{D^3}{d^2} = \frac{1}{\sqrt{2}\,\pi}\left(\frac{V_{\text{gas}}}{V_{\text{solid}}}\right)\frac{d^3}{d^2} = \frac{1}{\sqrt{2}\,\pi}\left(\frac{V_{\text{gas}}}{V_{\text{solid}}}\right)d$$

And so, we can obtain d if we can determine the free mean path, λ, by using

$$d = \sqrt{2}\,\pi\lambda\left(\frac{V_{\text{solid}}}{V_{\text{gas}}}\right) \tag{6}$$

3.2 Iodine diffusion

The concentration of molecules diffusing into a substance can be approximated by a Gaussian function of the distance. Since the concentration falls off so rapidly with distance, a reasonable estimate of the mean diffusion distance, S_{rms}, is one-half the distance to where the vapor becomes invisible. This distance can be determined by measuring the **time of diffusion**, Δt.

From Eq. (2), we can determine the number of collisions, N_{C}, a molecule will take during the time Δt:

$$\sqrt{N_{\text{C}}} = \frac{\langle v\rangle\Delta t}{\lambda}$$

Therefore, we can write Eq. (4) as

$$S_{\text{rms}} = \lambda\sqrt{\frac{\langle v\rangle\Delta t}{\lambda}} = \sqrt{\lambda\langle v\rangle\Delta t} \quad\Rightarrow\quad (S_{\text{rms}})^2 = \lambda\langle v\rangle\Delta t$$

and thus

$$\lambda = \frac{(S_{\text{rms}})^2}{\langle v\rangle\Delta t} \tag{7}$$

We can now use the Maxwell-Boltzmann distribution and replace $\langle v\rangle = \sqrt{8/3\pi}\,v_{\text{rms}}$, where the rms speed is $v_{\text{rms}} = \sqrt{3kT/M}$. So,

$$\langle v\rangle = \sqrt{\frac{8kT}{\pi M}} \tag{8}$$

Or in other words, $kT = (\pi/8)M\langle v\rangle^2$. Using the ideal gas law, we get

$$pV = NkT = N\left(\frac{\pi}{8}M\langle v\rangle^2\right) = \frac{\pi}{8}(NM)\langle v\rangle^2$$

or

$$pV = \frac{\pi}{8}m\,\langle v\rangle^2$$

where m is the mass of the whole sample, N is the number of molecules, and M is the molecular mass. Hence,

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

And, finally, we can use density $\rho = m/V$ to obtain

$$\langle v \rangle = \sqrt{\frac{8}{\pi}\frac{p}{\rho}} \tag{9}$$

Thus, we can use Eq. (7) to estimate the mean free path, λ, by observing the time of diffusion of iodine in air (Δt), using a mean diffusion distance of $S_{\text{rms}} = 1/2\ \text{diffusion length}$, and finding the mean speed through Eq. (9). We then proceed to determine a value for d from using Eq. (6), and thus a value for D from Eq. (5).

Finally, we use Avogadro's hypothesis to obtain Avogadro's number N_{A} by finding the ratio of the volume of one mole of gas, $V_{1-\text{mol}}$, to the volume of one molecule, D^3:

$$N_{\text{A}} = \mathcal{N} V_{1-\text{mol}} = \frac{V_{1-\text{mol}}}{D^3} \tag{10}$$

4 Materials

1. Iodine crystals.
2. Dry ice
3. 4 Test tubes, more than 10 cm tall.
4. Graduated 500 mL cylindrical beaker.
5. Thermometer
6. Hot plate.
7. Clamper and stand.
8. Small container.

5 Experimental Procedure

5.1 Initial measurements

1. Make a record of the room temperature, T_{room}, and the atmospheric pressure, p.

5.2 Iodine diffusion

1. A beaker is filled with water, and a few boiling chips and heated until the water begins to boil. After the boiling starts the heating rate is reduced to the minimum amount needed to sustain the boiling.
2. A dry 15 cm test tube is marked at 10 cm from its fused end. Most of it is inserted in the boiling water and clamped. Care is taken so that no water is allowed to get inside the tube. The empty test tube is left in the beaker for a few minutes to come to the temperature of the boiling water.
3. A few crystals of iodine are carefully dropped to the bottom of the test tube with the help of a small pair of tweezers. After the iodine is placed in the tube, its top is plugged tightly with a rubber stopper. The test tube is then immersed completely in the boiling water by being re-clamped from the extending part of the stopper.
4. As the crystals are inserted, start measuring the time (Δt) the purple vapor takes to diffuse upward. First, notice that after a minute or so, different shades of the purple color become clearly visible under regular lighting conditions. Take the time when the *faint purple* front reaches the 10 cm mark on the tube. During this time, the average diffusion length (the diffusion length of the *half purple* front) is 5 cm.
5. Repeat the procedure using other test tubes at least three more times.

5.3 Dry ice sublimation

1. Put a graduated beaker sideways in a plugged laboratory sink or a small bucket of water. Water is added until the beaker is fully covered and full of water. The beaker is then turned upside down, raised, and is put to rest with about 80% of its height above the water level.

2. Take a small piece of about 1–1½ g of dry ice and weigh it, working as fast as possible. Keep your piece covered within the plastic bag to avoid accumulation of regular (water) ice on it. Use rubber gloves when handling it. Do this measurement three times, breaking a fresh piece on every trial.
3. Once the mass is measured, quickly put the dry ice sample under the beaker, and support it by hand under water. It will slowly rise by itself away from the hand to the top of the water column inside the beaker and complete its sublimation.
4. After sublimation, the volume of the $\mathrm{CO_2}$ gas is measured by comparing the initial and final volumes of gas inside the beaker.
5. Finally, the volume of solid dry ice is found by combining the density of dry ice and the mass of the piece you weighed.

6 Analysis

6.1 Iodine diffusion–Mean free path estimate

1. Use the gas density of air at room temperature ($\rho = 1.2\ \mathrm{kg/m^3}$) and your measurement of atmospheric pressure inside Eq. (9) to find the mean molecular speed of air $\langle v_{\mathrm{air}} \rangle$.
2. From Eq. (8), write relations for the mean molecular speeds of air and iodine, at room temperature (constant temperature), by finding:

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi M}} \Rightarrow M \langle v \rangle^2 = \frac{8kT}{\pi M}$$

The right side is a constant, so we get that $M_{\mathrm{air}} \langle v_{\mathrm{air}} \rangle^2 = M_{\mathrm{iodine}} \langle v_{\mathrm{I-room}} \rangle^2$. Thus,

$$\boxed{\langle v_{\mathrm{I-room}} \rangle = \sqrt{\frac{M_{\mathrm{air}}}{M_{\mathrm{iodine}}}} \langle v_{\mathrm{air}} \rangle}$$

Using the ratio for molecular mass between air and iodine, $M_{\mathrm{air}}/M_{\mathrm{iodine}} = (28.6/254) = 0.1126$, find the mean molecular speed of iodine at room temperature, $\langle v_{\mathrm{I-room}} \rangle$.

3. Again, use Eq. (8) for iodine at room temperature and that at the temperature inside the test tube, $T_{\mathrm{I-tube}}$. This time, temperature changes but the mass remains the same, so

$$\frac{\langle v \rangle^2}{T} = \frac{8k}{\pi M}$$

The right side is a constant, so we get:

$$\frac{\langle v_{\mathrm{I-tube}} \rangle^2}{T_{\mathrm{I-tube}}} = \frac{\langle v_{\mathrm{I-room}} \rangle^2}{T_{\mathrm{room}}}$$

$$\boxed{\langle v_{\mathrm{I-tube}} \rangle = \sqrt{\frac{T_{\mathrm{I-tube}}}{T_{\mathrm{room}}}} \langle v_{\mathrm{I-room}} \rangle}$$

You can now calculate the mean molecular speed of iodine, $\langle v_{\mathrm{I-tube}} \rangle$, at $T_{\mathrm{I-tube}}$ (in kelvin).

4. As mentioned above, the average diffusion length (S_{rms}) is half the distance traveled by iodine at the time recorded (Δt), i.e., $S_{\mathrm{rms}} = 5\ \mathrm{cm}$. Using this value, and Eq. (7), find the free mean path (λ).

6.2 Dry ice sublimation–Molecular density estimate

1. Using the density of solid dry ice ($\rho = 1500\ \mathrm{kg/m^3}$), find its volume ($V_{\mathrm{S}}$) for every mass measured (m_{S}), and their average.
2. Fin the average volume of $\mathrm{CO_2}$ (V_{g}) for the three trials measured during the experiment.
3. Using the average volume of $\mathrm{CO_2}$ (V_{g}) and the average volume of solid dry ice (V_{S}), find their ratio $V_{\mathrm{S}}/V_{\mathrm{G}}$, and then find the molecular diameter (d) by using Eq. (6).

4. Once *d* is found, use Eq. (5) to find the molecular density $\mathcal{N} = 1/D^3$.

6.3 Avogadro's number

1. Using the ideal gas law, find the volume of a mole, $V_{1-\mathrm{mol}}$, at the current room's temperature and pressure conditions.
2. Now use Avogadro's hypothesis, and the volume of a mole found in step 1, to obtain Avogadro's number by using Eq. (10).

7 Measurements

Table I – Initial Measurements		
Room T (K)	T_{room}	
Atmospheric p (Pa)	p	

Table II – Iodine Diffusion		
Trial	Δt (s)	$T_{\mathrm{I-tube}}$ (K)
1		
2		
3		
4		

Table III – Dry Ice Sublimation			
Trial	1	2	3
Mass of dry ice, m_S			
Volume of CO_2, V_G			

8 Calculations

8.1 Iodine diffusion–Mean free path estimate

Table IV		
Mean molecular speed of air.	v_{air}	
Mean molecular speed of iodine at T_{room}	$v_{\mathrm{I-room}}$	
Mean molecular speed of iodine ($T_{\mathrm{I-tube}}$)	$v_{\mathrm{I-tube}}$	
Free mean path	λ	

8.2 Dry ice sublimation–Molecular density estimate

Table V		
Volume of solid dry ice	V_S	
Volume of CO_2	V_g	
Molecular diameter	d	
Molecular density	$\mathcal{N} = 1/D^3$	

8.3 Avogadro's number and Boltzmann's constant

Table VI		
Volume of a mole of gas (T and P at current room's conditions.)	$V_{1-\mathrm{mol}}$	
Avogadro's number	N_{A}	

9 References

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