

Lecture 5 CH131 Summer 1

Wednesday, May 29, 2019

The will be lab today Wednesday, May 29

- Complete: Ideal gas law
- Partial pressures
- Kinetic theory of gases
- Practice with particle picture of gases

Next lecture: Continue 9.1–9.6: Calculation of molecular speeds; Distribution of speeds; How intermolecular attraction affects gas behavior; How molecular size affects gas behavior; Gas law for real gases: van der Waals equation



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[TP] The volume of a balloon filled with 1300 mol H₂(g) at 23 °C and 1 bar is ...
[Recall that R = 8.314 J / (K mol)]

- 0% 1. 2500 L
- 0% 2. 250,000 L
- 65% 3. 32,000 L
- 29% 4. 3,200,000 L
- 6% 5. None of the above

$$V = \frac{nRT}{P} = \frac{1300 \text{ mol} \times 8.314 \text{ J/(K mol)} \times 296 \text{ K}}{10^5 \text{ Pa}} = 32,000 \text{ L}$$

$$\left\{ \begin{aligned} P_a &= \frac{J}{m^3} \\ J &= P_a m^3 \end{aligned} \right. \quad \left\{ \begin{aligned} m^3 &= 10^3 \text{ L} \\ T &= 273.15 + 23 \end{aligned} \right.$$



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Using ideal gas law

22 L of He is stored at 152 bar and 31°C. How many balloons can each be filled with 5.0 L of He at 1.00 bar and 22 °C?

Answer: $k = 650$

$$x \times 5L = V_{\text{total}} = \frac{nRT_2}{P_2} = \frac{P_1 V_1}{RT_1} \cdot \frac{RT_2}{P_2} = \frac{P_1 V_1 T_2}{P_2 T_1} = \frac{152 \text{ bar} \times 22 \text{ L}}{1.00 \text{ bar} \times 304 \text{ K}} \times \frac{295 \text{ K}}{5 \text{ L}} = 650$$



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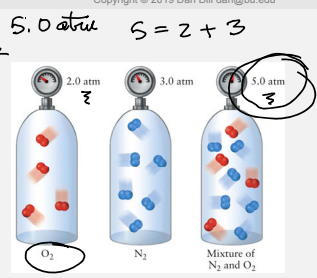
Mixtures of gases

Dalton's law of partial pressures

$$P_{O_2} = \frac{n_{O_2} RT}{V} \quad P_{N_2} = \frac{n_{N_2} RT}{V} \quad P = \frac{(n_{O_2} + n_{N_2}) RT}{V}$$

$$P_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{N_2}} P = x_{O_2} P$$

$$x_{O_2} + x_{N_2} = 1$$



$$\frac{n_{O_2}}{n_{O_2} + n_{N_2}} = x_{O_2}$$

$$\frac{n_{N_2}}{n_{O_2} + n_{N_2}} = x_{N_2}$$



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Mixtures of gases: Problem 9.33

33. Sulfur dioxide reacts with oxygen in the presence of platinum to give sulfur trioxide:

$$2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{SO}_3(\text{g})$$

Suppose that at one stage in the reaction, 26.0 mol SO₂, 83.0 mol O₂, and 17.0 mol SO₃ are present in the reaction vessel at a total pressure of 0.950 atm. Calculate the mole fraction of SO₃ and its partial pressure.

Handwritten notes:

$$P_{\text{SO}_3} = \chi_{\text{SO}_3} P$$

$$\chi_{\text{SO}_3} = \frac{17.0}{26.0 + 83.0 + 17.0} = 0.135$$

$$P_{\text{SO}_3} = 0.135 * 0.950 \text{ atm} = 0.128 \text{ atm}$$

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Kinetic-molecular theory of gases

$$P = \frac{nRT}{V}$$

Goal: Get microscopic expression for pressure P

Key idea 1: Pressure is due to force exerted by particles during collisions with the container walls

Key idea 2: Force is due to momentum change in collision with the container walls.

Note: Here upper-case P is used for pressure and lower-case p is used for momentum.

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Kinetic-molecular theory of gases

Handwritten derivations:

$$P = \frac{F}{A} \quad F = \frac{\Delta p}{\Delta t} \quad p = m u$$

$$\Delta p_{\text{part}} = p_f - p_i = -mu - (mu)$$

$$= -2mu$$

$$\Delta p_{\text{coll}} + \Delta p_{\text{part}} = 0 \text{ elastic.}$$

$$\Delta p_{\text{coll}} = -\Delta p_{\text{part}} = +2mu$$

$$F = \frac{\Delta p_{\text{coll}}}{\Delta t} = \frac{2mu}{\Delta t}$$

$$\Delta t = \frac{2L}{u}$$

$$F = \frac{2mu}{\frac{2L}{u}} = \frac{mu^2}{L}$$

Diagram: A cube of side length L . A particle with mass m and velocity u is shown colliding with a wall. The area of the wall is $A = L^2$. The volume is $V = L^3$.

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Kinetic-molecular theory of gases

Handwritten derivations:

$$F = \frac{\Delta p}{\Delta t} = \frac{2mu}{2L/u} = \frac{mu^2}{L}$$

$$P = \frac{F}{A} = \frac{F}{L^2} = \frac{mu^2}{L^3} = \frac{mu^2}{V}$$

$$PV = mu^2 = nRT$$

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Kinetic-molecular theory of gases

$$P_i = \frac{m u_i^2}{V}$$

$$P = P_1 + P_2 + \dots + P_N$$

$$= \frac{Nm}{V} \frac{(u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2)}{N}$$

of particles = N
 $= m N_A$

u_{avg}^2

total mass
 $Nm = m N_A m$
 $= m M$

$$P = \frac{Nm u_{\text{avg}}^2}{V} \Rightarrow P = \frac{m M u_{\text{avg}}^2}{3V}$$

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Kinetic-molecular theory of gases

$$P = \frac{m M u_{\text{avg}}^2}{3V} = \frac{m R T}{V}$$

$$u_{\text{avg}}^2 = \frac{3RT}{M}$$

$$= \frac{m M}{3V} \frac{3RT}{M}$$

heavies slower

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Kinetic-molecular theory of gases

Force due to j^{th} particle of mass m and speed u_j is $\Delta p / \Delta t$...

$$\Delta p = 2mu_j \text{ (elastic collision)}$$

$$\Delta t = 2L/u_j \text{ (travel time to opposite wall and back)}$$

$$F = \Delta p / \Delta t = mu_j^2 / L$$

Pressure due to j^{th} particle of mass m and speed u_j ...

$$P_j = \frac{F}{\text{area}} = \frac{F}{L^2} = \frac{mu_j^2}{L^3} = \frac{mu_j^2}{V}$$

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Kinetic-molecular theory of gases

A single particle exerts a pressure

$$P_j = \frac{mu_j^2}{V}$$

The total pressure P due to all of the N particles in the container is

$$P = \frac{m}{V} (u_1^2 + u_2^2 + \dots + u_j^2 + \dots + u_N^2)$$

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[TP] The different of speeds, u_1, u_2 , etc., in a gas is due to ...

- 0% 1. collisions of gas particles with the walls of the container.
- 19% 2. collisions of gas particles with one another
- 0% 3. attractions between the particles of the gas and the particles of the walls of the container.
- 0% 4. attractions between the particles of the gas.
- 44% 5. 1 and 2
- 0% 6. 1 and 3
- 0% 7. 1, 2 and 3
- 38% 8. 1, 2, 3 and 4

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Distribution of molecular speeds

Here is what happens to the speeds of 20,000 particles, all initially at the same speed, after they each have undergone successive numbers of collisions.

Bonomo & Riggi, Am. J. Phys., Vol 52, p 54 (1984)

Maxwell-Boltzmann distribution of speeds

$u_{rms}^2 = \frac{3RT}{M}$
 $u_{rms} = \sqrt{\frac{3RT}{M}}$

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Kinetic-molecular theory of gases

We can rewrite the total pressure due to the N particles,

$$P = \frac{m}{V}(u_1^2 + u_2^2 + \dots + u_j^2 + \dots + u_N^2)$$

in terms of the **average squared speed**

$$u_{avg}^2 = (u_1^2 + u_2^2 + \dots + u_j^2 + \dots + u_N^2)/N$$

by multiplying and dividing P by N ,

$$P = \frac{m}{V}N(u_1^2 + u_2^2 + \dots + u_j^2 + \dots + u_N^2)/N$$

$$= \frac{m}{V}Nu_{avg}^2 = \frac{m}{V}N_A n u_{avg}^2 = \frac{M}{V}n u_{avg}^2$$

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Kinetic-molecular theory of gases

The expression for pressure,

$$P = \frac{nM}{V}u_{avg}^2 \text{ (one dimension)}$$

assumes the particle **moves in just one dimension**, back and forth between opposite walls, say the walls perpendicular to the x axis.

A more detailed treatment that takes into account motion in all **three dimensions** shows that the pressure on any one wall is **only 1/3 as great**,

$$P = \frac{nM}{3V}u_{avg}^2 \text{ (three dimensions)}$$

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Calculation of molecular speeds

We now have two expressions for pressure:

The **microscopic** expression $P = \frac{nMu_{\text{avg}}^2}{3} / V$

and the **macroscopic** expression $P = nRT / V$

Comparing these, we get that $\frac{Mu_{\text{avg}}^2}{3} = RT \dots$

and so that the average squared speed is $u_{\text{avg}}^2 = \frac{3RT}{M}$



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Calculation of molecular speeds

$$u_{\text{avg}}^2 = \frac{3RT}{M}$$

is the connection between...

microscopic **motion**, quantified as u_{avg}^2 , and ...

the macroscopic concept **temperature**, T , and molar **mass**, M .

The square **root** of the **mean** (average) **squared** speed is the **rms speed** ...

$$u_{\text{rms}} = \sqrt{u_{\text{avg}}^2} = \sqrt{\frac{3RT}{M}}$$



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Practice with particle picture of gases

Let's consider some questions to develop a **particle-level understanding** of why gases behave the way they do.



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[TP] Gas pressure is due to ...

- 94% 1. collisions of gas particles with the walls of the container.
- 6% 2. collisions of gas particles with one another
- 0% 3. attractions between the particles of the gas and the particles of the walls of the container.
- 0% 4. attractions between the particles of the gas.
- 0% 5. 1 and 2
- 0% 6. 1 and 3
- 0% 7. 1, 2 and 3
- 0% 8. 1, 2, 3 and 4



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[Quiz] A container of volume V is filled with a gas at 20°C . If V is decreased (while keeping T constant), the pressure P exerted by the gas on the walls of the container goes up ($P = nRT/V$). Why?

- 6% 1. The particles move faster
- 0% 2. The particles move slower
- 0% 3. The particles hit the walls harder
- 0% 4. The particles hit the walls less hard
- 94% 5. The particles hit the walls more often
- 0% 6. The particles hit the walls less often



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[TP] When more particles are added to the same V at the same T , P goes up ($P = nRT/V$). Why?

- 0% 1. The particles move faster
- 0% 2. The particles move slower
- 0% 3. The particles hit the walls harder
- 0% 4. The particles hit the walls less hard
- 100% 5. More particles hit the walls in a given time
- 0% 6. Fewer particles hit the wall in a given time



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[TP] When a gas is heated, if the P is to remain constant, then volume V must go up ($P = nRT/V$). Why?

- 0% 1. The particles move faster
- 0% 2. The particles move slower
- 0% 3. The particles hit the walls harder
- 0% 4. The particles hit the walls less hard
- 100% 5. The distance travelled between collisions must increase
- 0% 6. The distance travelled between collisions must decrease



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[TP] Two 1 L containers, A and B, each contain equal numbers of particles at 20°C . The particles of gas in A are twice as heavy as those in B. What are the relative pressures in the two containers?

- 0% 1. Pressure of A is half the pressure of B
- 100% 2. Pressure of A equals the pressure of B
- 0% 3. Pressure of A is twice the pressure of B
- 0% 4. Pressure of A is four times the pressure of B



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Practice with particle picture of gases

Two 1 L containers, A and B, each contain equal numbers of particles at 20 °C. The particles of gas in A are twice as heavy as those in B. The pressure in the two containers is **the same**.

How can this be?

$$P = (nM/V) \frac{1}{3} u_{avg}^2 = (nM/V) \frac{1}{3} (3RT/M)$$

Pressure depends on **speed AND mass**

Heavy particles move **s l o w l y !!!**

Light particles move **q u i c k l y !!!**

But at the **same temperature**, they exert the same pressure.



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[TP] Equal amounts of gases A and B are in a single container. The mass of a molecule of gas in A is **twice** that of the gas in B, $m_A = 2 m_B$. The container is pierced with a hole **0.003 mm** in diameter.

When 5 minutes has elapsed after the piercing, the container will contain ...

- 88% 1. more A than B
- 6% 2. equal amounts of each gas
- 0% 3. less A than B
- 6% 4. Further information needed



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