Lecture 36

Equations of state.

The ideal gas.

Kinetic model of a gas.

ACT: Coin and mulch

A piece of wood and a coin initially at 10°C are left out in the sun until they are both at the outside temperature (35°C). As you know, if you pick them up and hold them in your hand, the coin feels warmer. Why is that?

A. Because the specific heat of the metal is larger than that of wood.

B. Because the thermal conductivity of the metal is larger than that of wood.

C. Because the metal absorbed more heat than the wood.

$c_{wood} > c_{metal}$ It takes more heat to raise the temperature of wood.
But this has nothing to do with how warm something feels…

Something *feels* warm when heat is transferring to your skin.

$k_{wood} < k_{metal}$ Heat transfer rate is higher for metal.

→ More heat is transferred to your skin in a given Δt for metals.

State variables

State variables for a system: they characterize the system macroscopically at a given time.

- Pressure
- Temperature
- Volume
- Mass or moles

Important: a system is in a thermal state that can be described by these variables when ALL the system has uniform pressure, temperature, etc.

Example: Gas in a tube whose ends are kept at different temperature is NOT in a thermal state.

Equation of state

The equation of state relates the state variables.

Can be obtained:

- Empirically
- From statistical mechanics

The ideal gas

An ideal gas is one whose molecules

- are very small (point-like)
- do not interact with one another

This is very true for any gas that is not in an "extreme" situation.
The gas is NOT ideal if we have:

- high density
- high pressure
- near transition to liquid (or solid)
- molecules are very large

The ideal gas state equation

$$\boxed{pV = nRT}$$

n = number of moles

$$R = 8.31\ \frac{\text{J}}{\text{mol}\cdot\text{K}} = 0.082\ \frac{\text{liter}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$$

Ideal gas constant

Example: Volume of ideal gas at STP

STP = Standard Temperature and Pressure = 0°C and 1 atm

What is the volume of one mole of an ideal gas at STP?

$$V = \frac{nRT}{p} = \frac{(1\ \text{mole})\left(8.31\frac{\text{J}}{\text{mol K}}\right)(273.15\ \text{K})}{1.01\times10^{5}\ \text{Pa}} = 0.00224\ \text{m}^3 = \boxed{22.4\ \text{liters}}$$

For any ideal gas

Partial pressure

If we have a mix of two gases A and B in a volume V, we can still use the ideal gas equation as long as they are both dilute.

They both have the same T and occupy the entire V

$p_X V = n_X RT$ for x = A, B p_X = partial pressure of gas X

Just like $n_{all} = n_A + n_B$, $p_{all} = p_A + p_B$

$$\frac{p_B}{n_B} = \frac{p_A}{n_A} \quad \left(= \frac{RT}{V}\right)$$

$$\boxed{p_X = \frac{n_X}{n_{all}} p_{all}}$$

It makes sense: pressure comes from collisions with the wall.

$\frac{n_X}{n_{all}}$ is the fraction of collisions with molecules of gas X.

Kinetic model of a monoatomic ideal gas

Let us try to link this macroscopic model with a microscopic description of the system.

Model assumptions

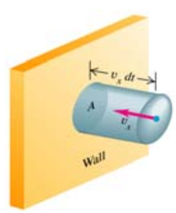
- container with volume V, a large number of molecules (N), each molecule has mass m
- molecules behave as point particles, occupy no volume and do not interact with one another.
- molecules are in constant motion, obey Newton's Laws and collide elastically with walls.
- container walls are perfectly rigid and do not move.

Strategy

1. Calculate number of collisions (per unit time) of molecules hitting wall (area A)
2. Calculate the momentum change of the molecules due to these collisions
3. Find the force exerted by the wall on gas that causes this momentum change
4. Use Newton 3rd law to get force exerted by gas on the wall
5. Pressure = (force exerted by gas on wall)/area
6. Use this to get/understand $pV=nRT$ (Microscopic expression for p, T)

Step 1: Number of collisions

$|v_x|$ = magnitude of x-component of molecule's velocity (for now assume all molecules have the same $|v_x|$



If a molecule is going to hit the wall in the time interval dt

–it must be within a distance $|v_x|\,dt$ from the wall

ie, within cylinder of volume $A|v_x|dt$

–within this distance, half of molecules going toward wall, half moving away

$$\text{number molecules hitting wall in } dt = \frac{1}{2}(\text{volume})(\text{density of molecules})$$
$$= \frac{1}{2}\left(A|v_x|dt\right)\left(\frac{N}{V}\right)$$

Step 2: Change in momentum

Elastic collisions with an unmovable wall:
The *x*-component of molecule's velocity changes from v_x to $-v_x$

$$|\Delta p_x| = 2m|v_x| \qquad (m = \text{mass of a molecule})$$

For all the molecules impacting area A of wall in dt:

$$|dP_x| = \frac{1}{2}(A|v_x|dt)\left(\frac{N}{V}\right)2m|v_x| = \frac{NAmv_x^2}{V}dt$$

Step 3: Force exerted by wall

$$|F_{x,\text{ on wall}}| = \frac{|dP_x|}{dt} = \frac{NAmv_x^2}{V}$$

Step 4: Force exerted on wall

$$|F_{x,\text{ by wall}}| = |F_{x,\text{ on wall}}|$$
(Newton's 3rd)

Step 5: Pressure

$$p = \frac{|F_{x,\text{ on wall}}|}{A} = \frac{Nmv_x^2}{V}$$

Step 6: Link to ideal gas equation

$$pV = Nmv_x^2$$
macroscopic (pV) — microscopic (Nmv_x^2)

Problem: Who knows what is v_x for each molecule??

Additional step: Averages

$$\langle pV\rangle = \langle Nmv_x^2\rangle \longrightarrow pV = Nm\langle v_x^2\rangle$$

$$3D: \quad v^2 = v_x^2 + v_y^2 + v_z^2 \longrightarrow \langle v^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle$$

All directions are the same, so $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = \frac{\langle v^2\rangle}{3}$

Thus, $$pV = \frac{1}{3}Nm\langle v^2\rangle = \frac{2}{3}N\left(\frac{1}{2}m\langle v^2\rangle\right) = \frac{2}{3}N\langle KE_{\text{translation}}\rangle$$

$$\boxed{pV = \frac{2}{3}\langle\text{total translational kinetic energy of molecules}\rangle}$$

Microscopic interpretation of temperature (finally justified)

$$\left.\begin{aligned} pV &= nRT \\ pV &= \frac{2}{3}N\left(\frac{1}{2}m\langle v^2\rangle\right)\end{aligned}\right\} \quad \frac{3}{2}nRT = N\frac{1}{2}m\langle v^2\rangle$$

$n = \frac{N}{N_A}$ where $\boxed{N_A = 6.022\times10^{23}}$ Avogadro's number

Define $\boxed{k = \frac{R}{N_A} = 1.38\times10^{-23}\ \text{J/K}}$ Boltzmann's constant

$$\boxed{\frac{3}{2}kT = \frac{1}{2}m\langle v^2\rangle}$$
Average kinetic energy of one molecule (for monoatomic ideal gas)

ACT: Molecular speeds

Two separate containers of gas are in thermal equilibrium with each other. One contains He and the other contains Ar. Which of the following statements is correct?

A. $\langle v_{He}^2 \rangle = \langle v_{Ar}^2 \rangle$

B. $\langle v_{He}^2 \rangle > \langle v_{Ar}^2 \rangle$

C. $\langle v_{He}^2 \rangle < \langle v_{Ar}^2 \rangle$

$\langle K \rangle = \frac{3}{2}kT$ They have the same average kinetic energy.

$\frac{1}{2}m\langle v^2 \rangle = \frac{3}{2}kT$ The heavier mass must have slower speeds.

Root-mean-square velocities

The key quantity is $\langle v^2 \rangle$ → mean of squared velocities

Take the square-root → back to the units of velocity

$$v_{rms} = \sqrt{\langle v^2 \rangle}$$

$$\frac{1}{2}mv_{rms}^2 = \frac{3}{2}kT$$

Example: 3 molecules at 400,500,600 ms^{-1}

$$\text{average} = \frac{400+500+600}{3} = 500 \text{ m/s}$$

$$\text{rms} = \sqrt{\frac{400^2+500^2+600^2}{3}} = 507 \text{ m/s}$$

Not the same!