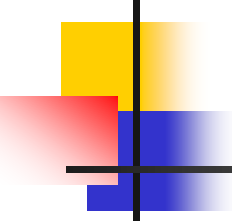




QUIZ #5

John BROWN, st. #391245

1. D
2. C
3. E
4. A



Please send (in seven minutes)
your answers as an email text

- to: athul066@uottawa.ca
- cc: stadnik@uottawa.ca



An Ideal Gas

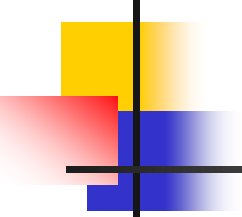
- For gases, the interatomic forces within the gas are very weak
 - We can imagine these forces to be nonexistent
- Note that there is no equilibrium separation for the atoms
 - Thus, no “standard” volume at a given temperature



An Ideal Gas

- For a gas, the volume is entirely determined by the container holding the gas
- Equations involving gases will contain the volume, V , as a variable
 - This is instead of focusing on ΔV

An Ideal Gas

- 
- It is useful to know how the volume, pressure and temperature of the gas of mass m are related
 - The equation that interrelates these quantities is called the **equation of state**
 - These are generally quite complicated
 - If the gas is maintained at a low pressure, the equation of state becomes much easier
 - The equation of state can be determined from experimental results
 - This type of a low density gas is commonly referred to as an **ideal gas**
 - The ideal gas model can be used to make predictions about the behavior of real gases at low pressures



The Mole

- The amount of gas in a given volume is conveniently expressed in terms of the number of moles
- One **mole** of any substance is that amount of the substance that contains **Avogadro's number** of constituent particles
 - Avogadro's number $N_A = 6.022 \times 10^{23}$
 - The constituent particles can be atoms or molecules



Moles

- The number of moles can be determined from the mass of the substance: $n = m/M$
 - M is the molar mass of the substance
 - m is the mass of the sample
 - n is the number of moles

Ideal Gas Experiment

- Suppose an ideal gas is confined to cylindrical container
- The volume can be varied by means of a movable piston
- Assume the cylinder does not leak (the mass of the gas remains constant)
- Experiments determine a great deal of information about the gas





Gas Laws

- When a gas is kept at a constant temperature, its pressure is inversely proportional to its volume (**Boyle's law**) – **demo** (balloon in pumped enclosure)
- When a gas is kept at a constant pressure, its volume is directly proportional to its temperature (**Charles law**) – **demo** (LN poured on balloon)
- When the volume of the gas is kept constant, the pressure is directly proportional to the temperature (**Guy-Lussac's law**)



Ideal Gas Law

- The equation of state for an ideal gas combines and summarizes the other gas laws

$$PV = nRT$$

- This is known as the **ideal gas law**
- R is a constant, called the **Universal Gas Constant**
 - $R = 8.314 \text{ J/mol}\cdot\text{K} = 0.08214 \text{ L}\cdot\text{atm/mol}\cdot\text{K}$
- From this, you can determine ($V = nRT/P$) that 1 mole of any gas at atmospheric pressure and at 0°C is **22.4 L**

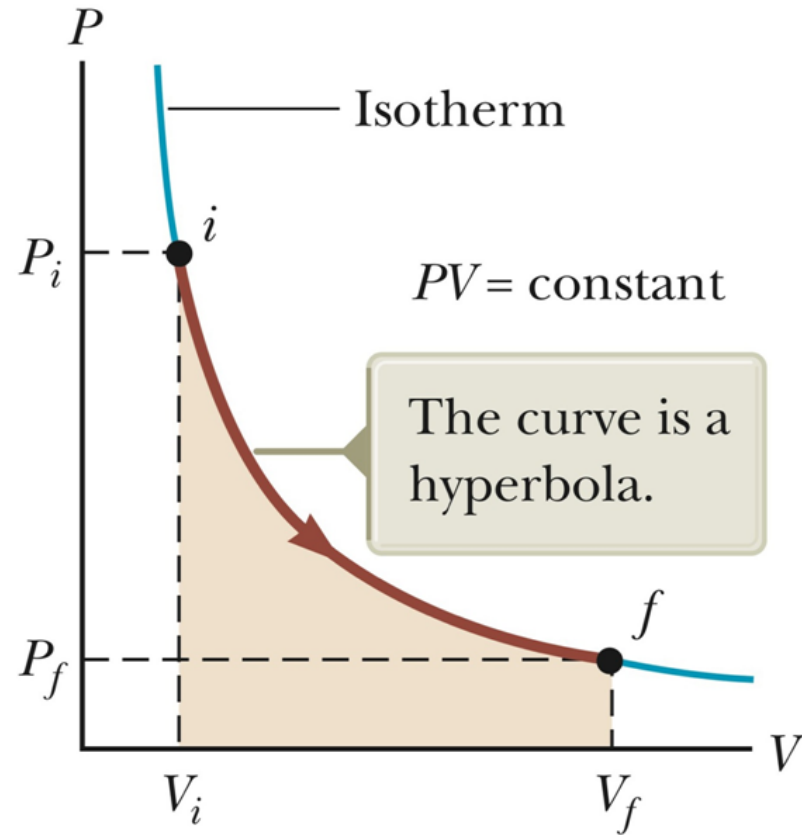


Ideal Gas Law

- The ideal gas law is often expressed in terms of the total number of molecules, N , present in the sample
- $PV = nRT = (N/N_A)RT = Nk_B T$
 - k_B is Boltzmann's constant; $k_B = R/N_A$
 - $k_B = 1.38 \times 10^{-23} \text{ J/K}$
- It is common to call P , V , and T the **thermodynamic variables** of an ideal gas

Isothermal Expansion of an Ideal Gas

- At right is a PV diagram of an isothermal expansion
- The curve is a hyperbola
- The equation of the curve is $PV = nRT = \text{constant}$
- The curve is called an **isotherm**



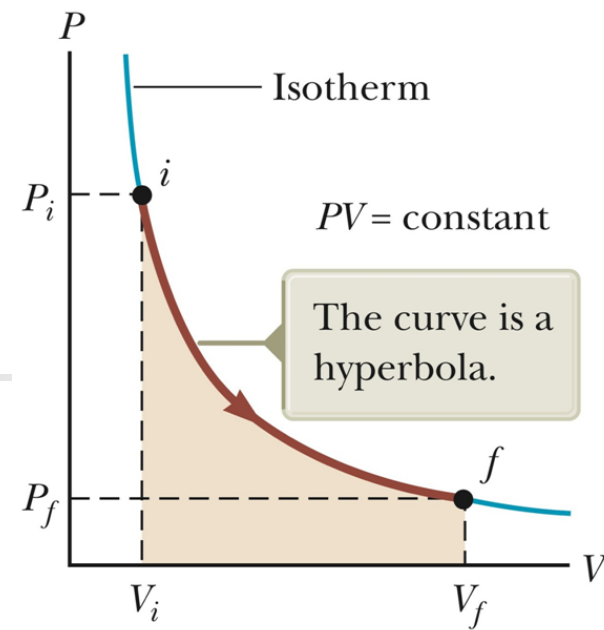
Isothermal Expansion

$$pV = nRT$$

- Because it is an ideal gas and the process is quasi-static, the ideal gas law is valid for each point of the path
- The work done by the gas in the expansion from state i to state f is

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

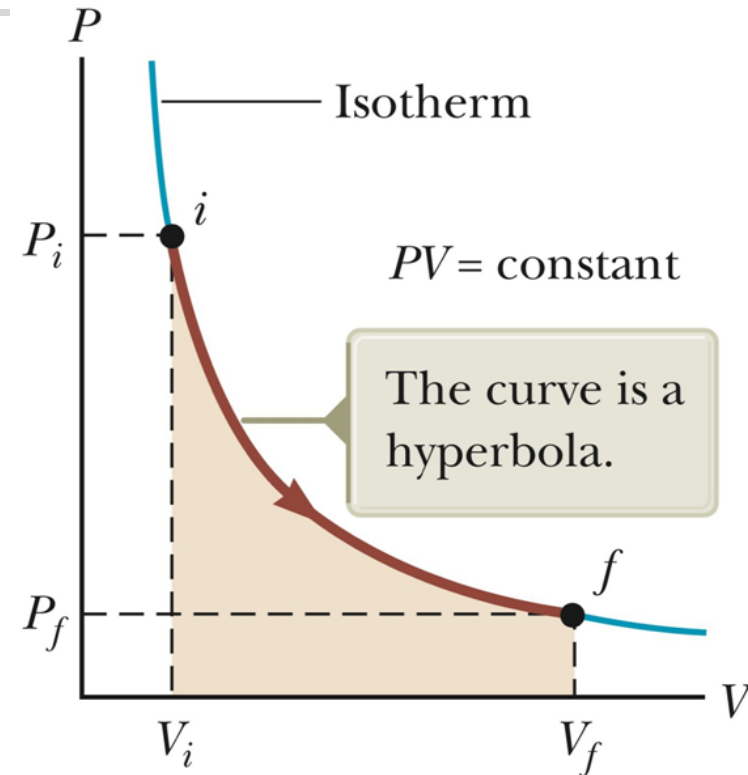
$$W = nRT \ln \left(\frac{V_f}{V_i} \right)$$



Isothermal Expansion

$$W = nRT \ln \left(\frac{V_f}{V_i} \right)$$

- Numerically, the work equals the area under the PV curve
 - The shaded area in the diagram
- If the gas expands, $V_f > V_i$ and the work done by the gas is positive
- If the gas is compressed, $V_f < V_i$ and the work done on the gas is negative



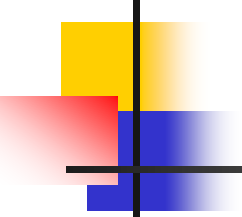
$$T = \text{constant} \rightarrow \Delta U = 0 \rightarrow Q = W$$



Films

- 16-07 (Brownian Motion)
- 16-08 (Brownian Motion Simulation)

Macroscopic vs. Microscopic Descriptions

- 
- So far we have dealt with **macroscopic** variables:
 - Pressure
 - Volume
 - Temperature
 - These can be related to a description on a **microscopic** level
 - Matter is treated as a collection of molecules
 - Applying Newton's laws of motion in a statistical manner to a collection of particles provides a reasonable description of thermodynamic processes
 - Pressure and temperature relate directly to molecular motion in a sample of gas

Ideal Gas Assumptions



- The number of molecules in the gas is large, and the average separation between the molecules is large compared with their dimensions
 - The molecules occupy a negligible volume within the container
 - This is consistent with the macroscopic model where we assumed the molecules were point-like



Ideal Gas Assumptions

- The molecules obey Newton's laws of motion, but as a whole they move randomly
 - Any molecule can move in any direction with any speed
- The molecules interact only by short-range forces during elastic collisions
 - This is consistent with the macroscopic model, in which the molecules exert no long-range forces on each other
- The molecules make elastic collisions with the walls
 - These collisions lead to the macroscopic pressure on the walls of the container
- The gas under consideration is a pure substance
 - All molecules are identical

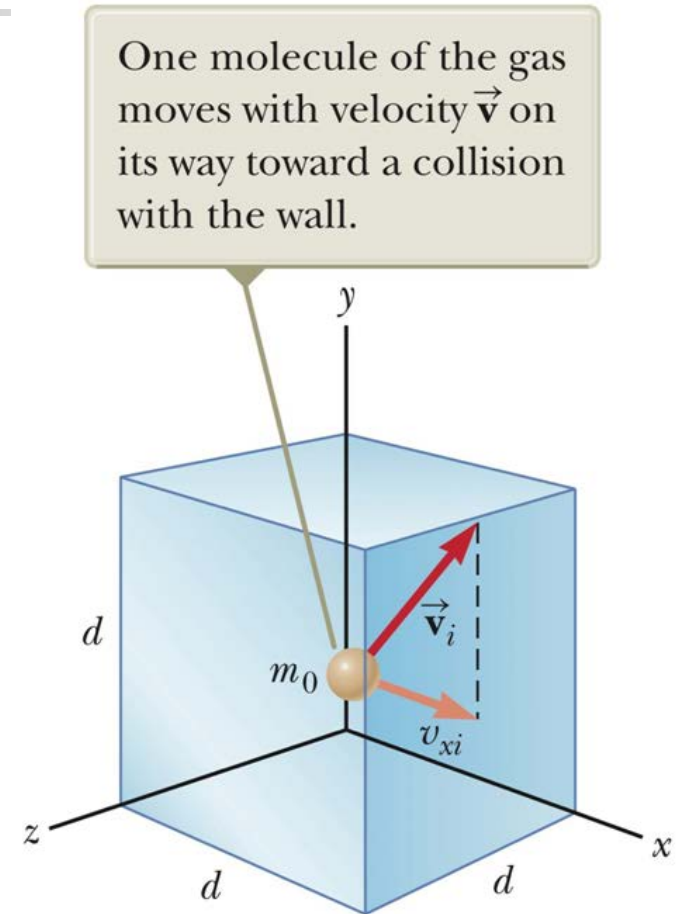


Ideal Gas Notes

- An ideal gas is often pictured as consisting of single atoms
- However, the behavior of molecular gases approximate that of ideal gases quite well
 - At low pressures
 - Molecular rotations and vibrations have no effect, on average, on the motions considered

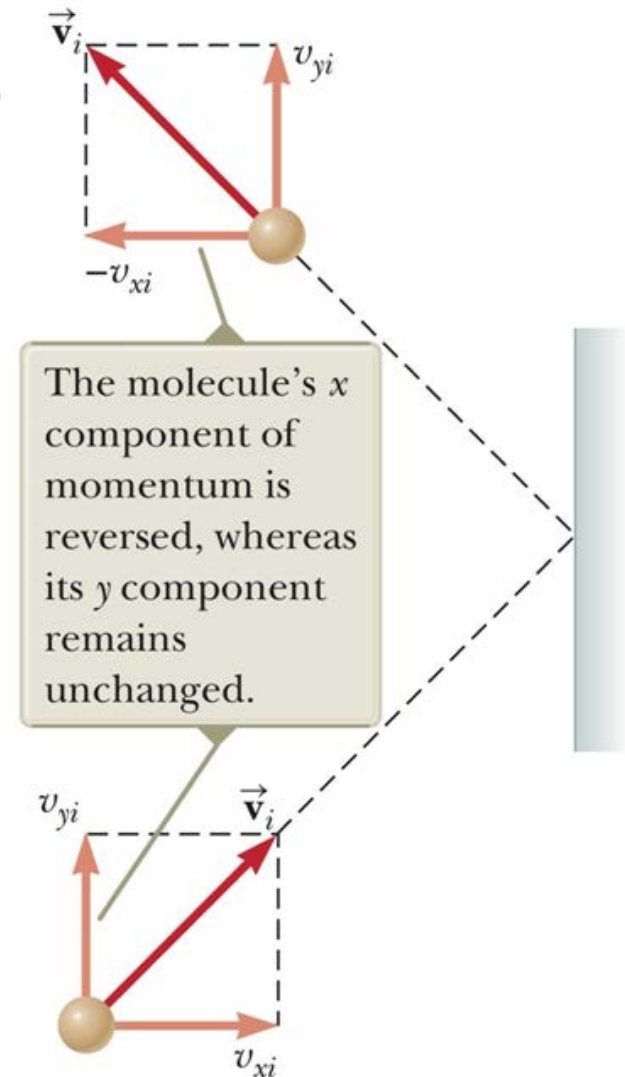
Pressure and Kinetic Energy

- Assume a container is a cube
 - Edges are of length d
- Look at the motion of the molecule in terms of its velocity components
- Look at its momentum and the average force



Pressure and Kinetic Energy

- Assume perfectly elastic collisions with the walls of the container
- The molecule's velocity component perpendicular to the wall is reversed
 - The mass of the wall is much greater than the mass of the molecule
- The impulse from the wall causes a change in the molecule's momentum



Pressure and Kinetic Energy

$$\Delta p_{xi} = -m_0 v_{xi} - (m_0 v_{xi}) = -2m_0 v_{xi}$$

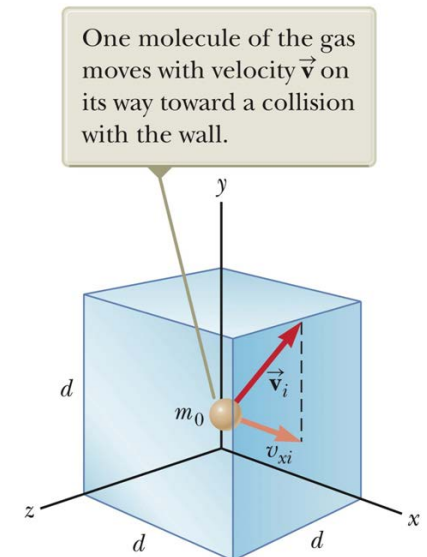
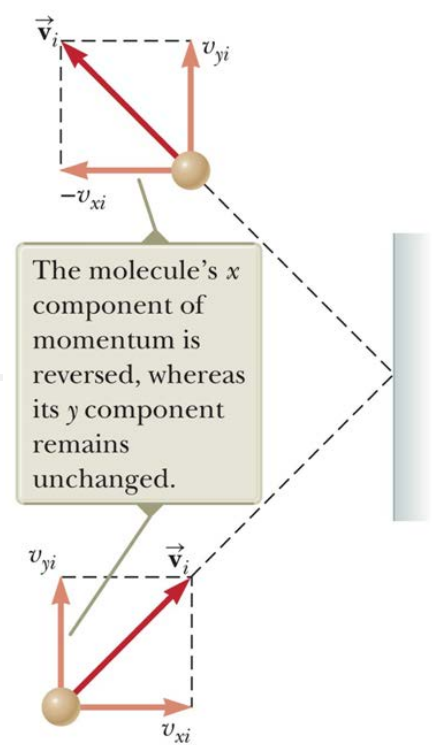
$$\overline{F}_{i,\text{on molecule}} \Delta t_{\text{collision}} = \Delta p_{xi} = -2m_0 v_{xi}$$

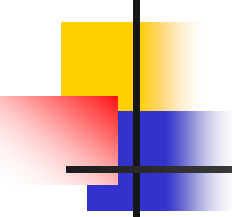
- The time interval between two collisions with the same wall is

$$\Delta t = \frac{2d}{v_{xi}}$$

$$\overline{F}_i \Delta t = -2m_0 v_{xi}$$

- \overline{F}_i is the average force component over the time interval for the molecule to move across the cube and back





$$\Delta t = \frac{2d}{v_{xi}}$$

$$\bar{F}_i \Delta t = -2m_0 v_{xi}$$

$$\bar{F}_i = -\frac{2m_0 v_{xi}}{\Delta t} = -\frac{2m_0 v_{xi}^2}{2d} = -\frac{m_0 v_{xi}^2}{d}$$

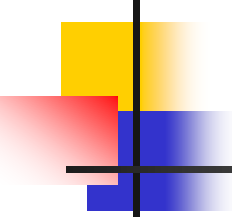
- Newton's third law:

$$\bar{F}_{i, \text{on wall}} = -\bar{F}_i = -\left(-\frac{m_0 v_{xi}^2}{d}\right) = \frac{m_0 v_{xi}^2}{d}$$

$$\bar{F} = \sum_{i=1}^N \frac{m_0 v_{xi}^2}{d} = \frac{m_0}{d} \sum_{i=1}^N v_{xi}^2$$

- For a very large number of molecules, $\bar{F} = F = \text{constant}$

$$F = \frac{m_0}{d} \sum_{i=1}^N v_{xi}^2$$



$$F = \frac{m_0}{d} \sum_{i=1}^N v_{xi}^2$$

$$\overline{v_x^2} = \frac{\sum_{i=1}^N v_{xi}^2}{N} \rightarrow \sum_{i=1}^N v_{xi}^2 = N \overline{v_x^2}$$

$$F = \frac{m_0}{d} N \overline{v_x^2}$$

$$v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2$$

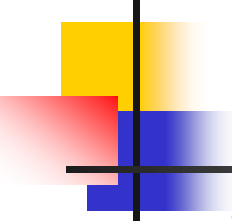
The average value of v^2 for all the molecules:

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

The motion is isotropic $\rightarrow \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$

$$\overline{v^2} = 3 \overline{v_x^2}$$

$$F = \frac{1}{3} N \frac{m_0}{d} \overline{v^2}$$

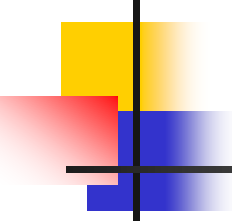

$$F = \frac{1}{3} N \frac{m_0}{d} \overline{v^2}$$

$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3} N \frac{m_0}{d^3} \overline{v^2} = \frac{1}{3} \left(\frac{N}{V} \right) m_0 \overline{v^2}$$

$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m_0 \overline{v^2} \right)$$

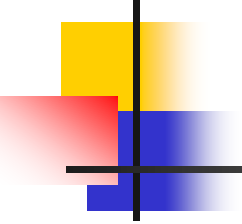
- The pressure is proportional to the number of molecules per unit volume (N/V) and to the average translational kinetic energy of the molecules
- This equation also relates the macroscopic quantity of pressure with a microscopic quantity of the average value of the square of the molecular speed

Pressure and Kinetic Energy


$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m_0 \overline{v^2} \right)$$

- One way to increase the pressure is to increase the number of molecules per unit volume (e.g., adding air to a tire)
- The pressure can also be increased by increasing the speed (kinetic energy) of the molecules
 - That can be accomplished by raising the temperature of the gas (e.g., continuous flexing of the tire as it moves along the road surface)

Molecular Interpretation of Temperature


$$P = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} m_0 \overline{v^2} \right)$$

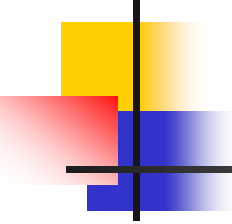
$$PV = \frac{2}{3} N \left(\frac{1}{2} m_0 \overline{v^2} \right) \rightarrow T = \frac{2}{3k_B} \left(\frac{1}{2} m_0 \overline{v^2} \right)$$
$$PV = Nk_B T$$

- The temperature is a direct measure of the average molecular kinetic energy

$$\frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

- The average translational kinetic energy per molecule is $\frac{3}{2} k_B T$

Molecular Interpretation of Temperature


$$\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}k_B T$$

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2}$$

$$\frac{1}{2}m_0\overline{v_x^2} = \frac{1}{2}k_B T \quad \frac{1}{2}m_0\overline{v_y^2} = \frac{1}{2}k_B T \quad \frac{1}{2}m_0\overline{v_z^2} = \frac{1}{2}k_B T$$

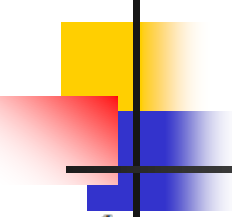
- Each translational degree of freedom contributes an equal amount to the energy of the gas, $\frac{1}{2}k_B T$
 - In general, a degree of freedom refers to an independent means by which a molecule can possess energy
- A generalization of this result is called the **theorem of equipartition of energy**



Theorem of Equipartition of Energy

- Each degree of freedom contributes $\frac{1}{2}k_{\text{B}}T$ to the energy of a system, where possible degrees of freedom are those associated with translation, rotation, and vibration of molecules

Total Kinetic Energy



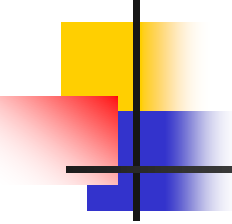
$$\frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

$$K_{\text{tot trans}} = N \left(\frac{1}{2} m_0 \overline{v^2} \right) = \frac{3}{2} N k_B T = \frac{3}{2} n R T$$

$$k_B = R/N_A \quad n = N/N_A$$

- If we have a gas with only translational energy, this is the *internal energy* of the gas
- This tells us that the internal energy of an ideal gas depends only on the temperature

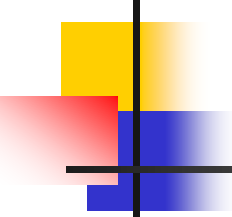
Root Mean Square (rms) Speed



$$\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}k_B T$$

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m_0}} = \sqrt{\frac{3RT}{M}}$$

- M is the molar mass and $M = m_0 N_A$
- At a given temperature, lighter molecules move faster, on the average, than heavier molecules
- Why is there no hydrogen in our atmosphere?



$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

Some Root-Mean-Square (rms) Speeds

Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)	Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)
H ₂	2.02	1902	NO	30.0	494
He	4.00	1352	O ₂	32.0	478
H ₂ O	18.0	637	CO ₂	44.0	408
Ne	20.2	602	SO ₂	64.1	338
N ₂ or CO	28.0	511			



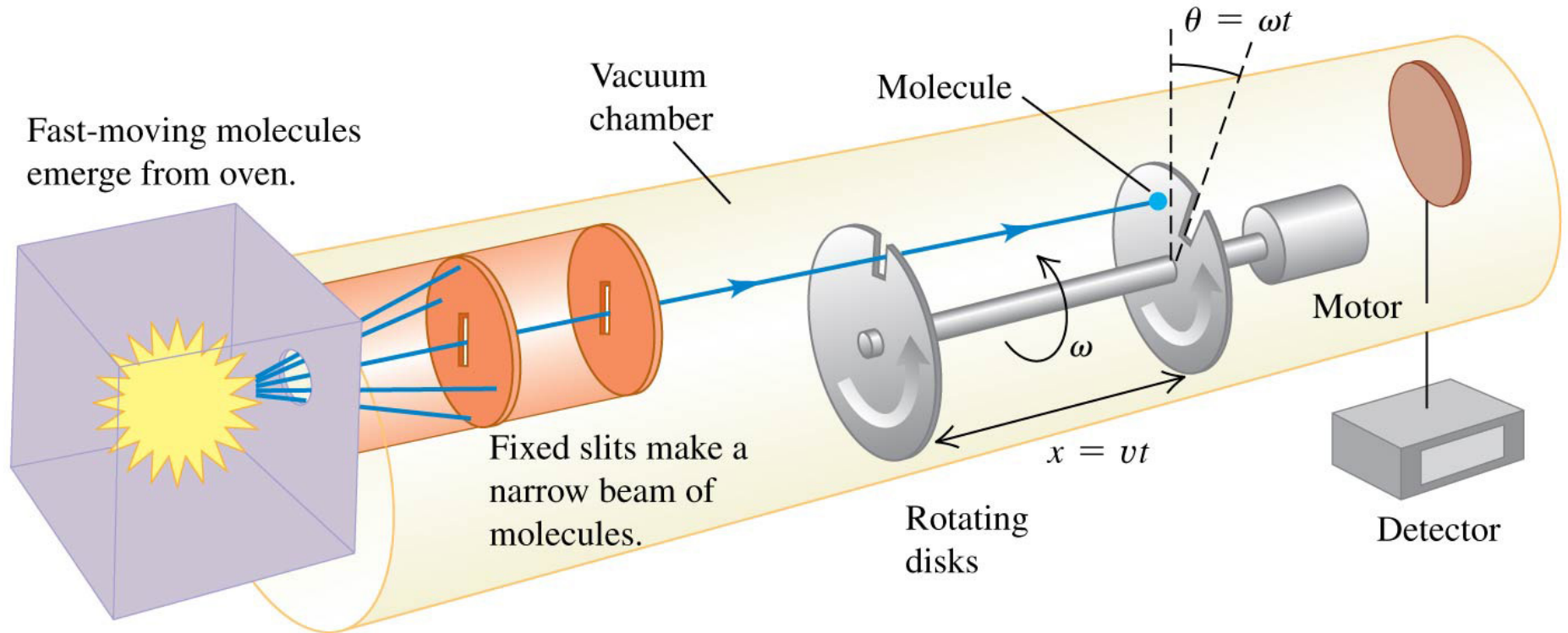
Boltzmann Distribution Law

- The motion of molecules is extremely chaotic
- Any individual molecule is colliding with others at an enormous rate
 - Typically at a rate of a billion times per second
- We add the **number density** $n_V(E)$
 - This is called a distribution function
 - It is defined so that $n_V(E)dE$ is the number of molecules per unit volume with energy between E and $E + dE$



Boltzmann Distribution Law

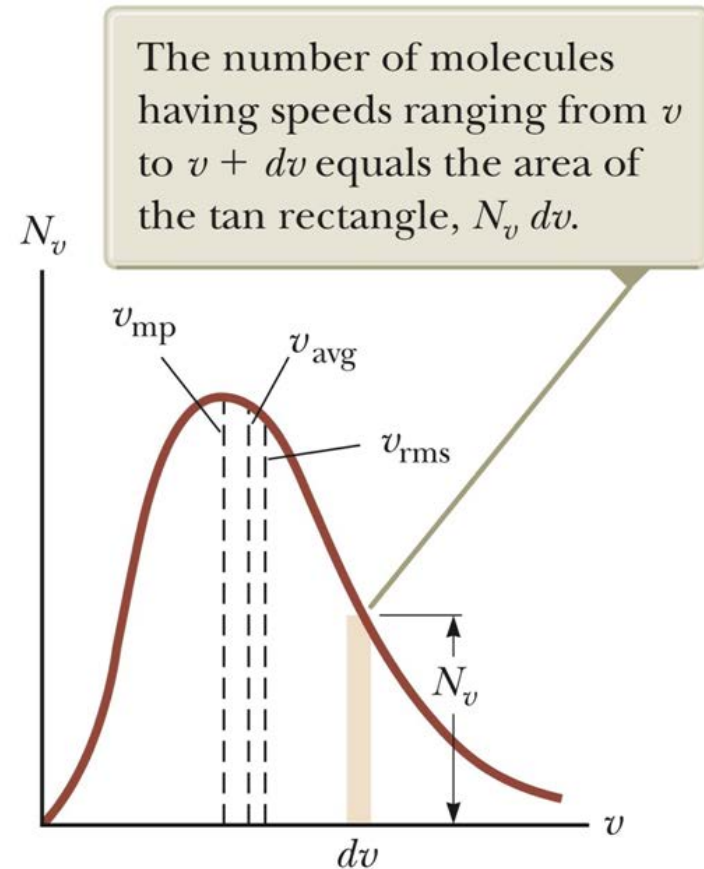
- From statistical mechanics, the number density is $n_V(E) = n_0 e^{-E/k_B T}$
- This equation is known as the Boltzmann distribution law
- n_0 is defined such that $n_0 dE$ is the number of molecules per unit volume having energy between $E = 0$ and $E = dE$
- It states that the probability of finding the molecule in a particular energy state varies exponentially as the negative energy divided by $k_B T$



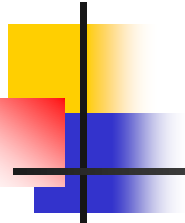
- A molecule with a speed v passes through the slit in the first rotating disk. When the molecule reaches second rotating disk, the disk have rotated through the offset angle θ . If $v = \omega x / \theta$, the molecule passes through the slit in the second rotating disk and reaches the detector. The disks function as a speed selector that passes only molecules within a certain narrow speed range (this range can be varied by changing ω). One can thus measure how many molecules lie within each of various speed ranges.

Distribution of Molecular Speeds

- The observed speed distribution of gas molecules in thermal equilibrium is shown at right
- N_v is called the **Maxwell-Boltzmann speed distribution function**
- If N is the total number of molecules, the number of molecules with speeds between v and $v + dv$ is $dN = N_v dv$



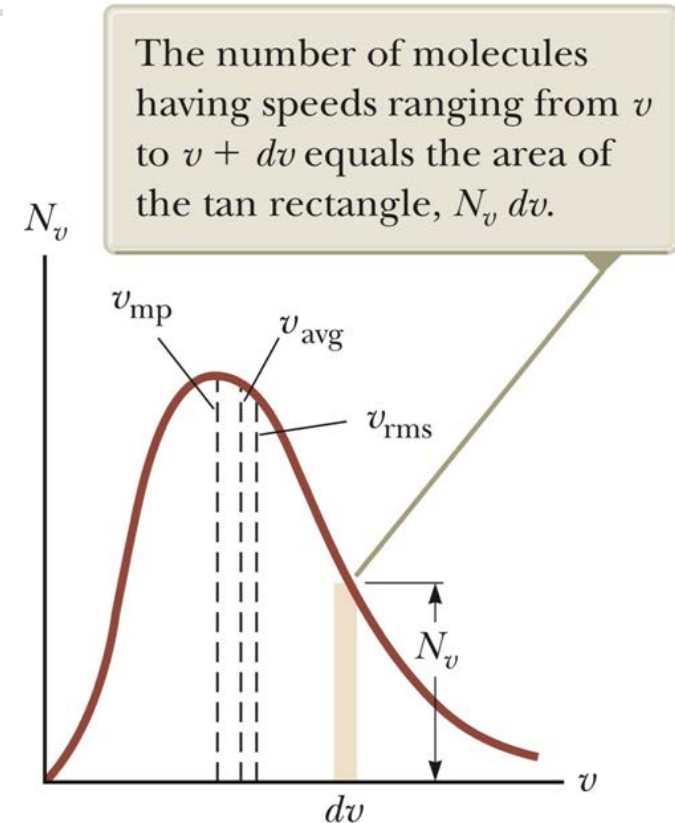
Maxwell-Boltzmann Speed Distribution Function

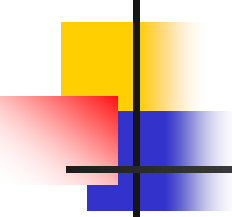


- The fraction of molecules with speeds between v and $v + dv$ is $(N_v dv)/N$
- This fraction is also equal to the probability that a molecule has a speed in the range v and $v + dv$

$$N_v = 4\pi N \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T}$$

- Note the appearance of the Boltzmann factor $e^{-E/k_B T}$ with $E = \frac{1}{2} m_0 v^2$




$$N_v = 4\pi N \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T}$$

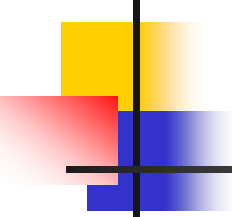
$$\overline{v^2} = \frac{1}{N} \int_0^\infty v^2 N_v dv \quad \text{Let } a = \frac{m_0}{2k_B T}$$

$$\overline{v^2} = \frac{(4N \pi^{-1/2} a^{3/2})}{N} \int_0^\infty v^4 e^{-av^2} dv$$

$$\int_0^\infty x^m e^{-ax^2} dx = \frac{\Gamma[(m+1)/2]}{2a^{(m+1)/2}}$$

$$\Gamma\left(m + \frac{1}{2}\right) = \frac{1 \cdot 3 \cdot 5 \cdots (2m-1)}{2^m} \sqrt{\pi} \quad m = 1, 3, 5, \dots$$

$$\int_0^\infty v^4 e^{-av^2} dv = \frac{\Gamma(5/2)}{2a^{5/2}} = \frac{\frac{3}{2^2} \sqrt{\pi}}{2a^{5/2}} = \frac{3\sqrt{\pi}}{8a^{5/2}}$$

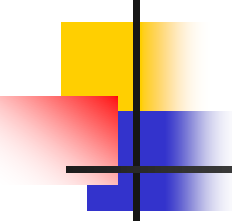

$$\overline{v^2} = \frac{(4N\pi^{-1/2}a^{3/2})}{N} \int_0^\infty v^4 e^{-av^2} dv$$

$$a = \frac{m_0}{2k_B T}$$

$$\int_0^\infty v^4 e^{-av^2} dv = \frac{\Gamma(5/2)}{2a^{5/2}} = \frac{\frac{3}{2^2}\sqrt{\pi}}{2a^{5/2}} = \frac{3\sqrt{\pi}}{8a^{5/2}}$$

$$\overline{v^2} = (4\pi^{-1/2}a^{3/2}) \frac{3\sqrt{\pi}}{8a^{5/2}} = \frac{3}{2a} = \frac{3k_B T}{m_0}$$

$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m_0}}$$



$$N_v = 4\pi N \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T}$$

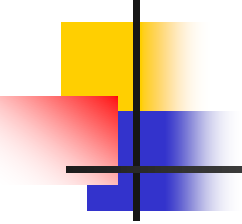
$$v_{\text{avg}} = \frac{1}{N} \int_0^\infty v N_v dv \quad \text{Let } a = \frac{m_0}{2k_B T}$$

$$v_{\text{avg}} = \frac{(4N \pi^{-1/2} a^{3/2})}{N} \int_0^\infty v^3 e^{-av^2} dv$$

$$\int_0^\infty x^m e^{-ax^2} dx = \frac{\Gamma[(m+1)/2]}{2a^{(m+1)/2}} \quad \Gamma(n+1) = n! \quad \text{if } n = 0, 1, 2, \dots$$

$$\int_0^\infty v^3 e^{-av^2} dv = \frac{\Gamma(2)}{2a^2} = \frac{1}{2a^2}$$

$$v_{\text{avg}} = (4\pi^{-1/2} a^{3/2}) \frac{1}{2a^2} = \frac{2\pi^{-1/2}}{a^{1/2}} = \sqrt{\frac{8k_B T}{\pi m_0}}$$


$$N_v = 4\pi N \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T}$$

- The most probable speed v_{mp} is the speed at which the distribution curve reaches the peak: $\frac{dN_v}{dv} = 0$

$$4\pi N \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} e^{-m_0 v^2 / 2k_B T} v \left(2 - \frac{2m_0 v^2}{2k_B T} \right) = 0$$

- Reject the solutions $v = 0$ and $v = \infty$ (they describe minimally probable speeds)

$$\left(2 - \frac{2m_0 v^2}{2k_B T} \right) = 0 \rightarrow v_{mp} = \sqrt{\frac{2k_B T}{m_0}}$$

$$M = m_0 N_A$$

$$k_B = R / N_A$$

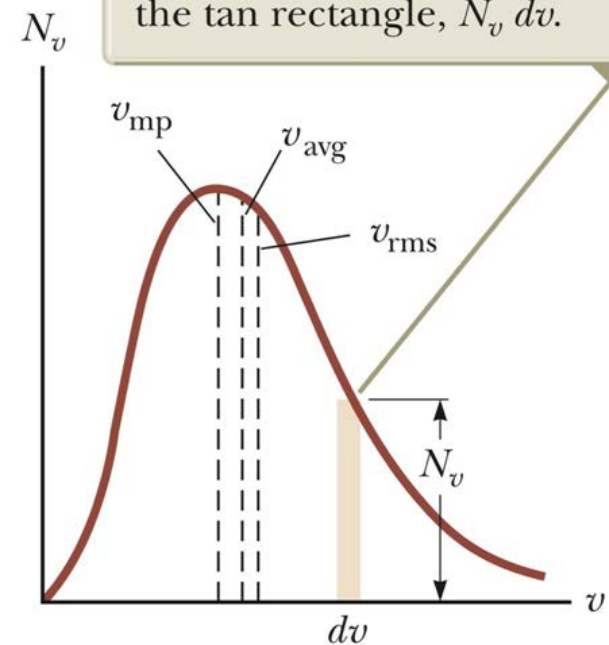
$$v_{\text{rms}} = \sqrt{\frac{3k_B T}{m_0}} = 1.73 \sqrt{\frac{k_B T}{m_0}} = 1.73 \sqrt{\frac{RT}{M}}$$

$$v_{\text{avg}} = \sqrt{\frac{8k_B T}{\pi m_0}} = 1.60 \sqrt{\frac{k_B T}{m_0}} = 1.60 \sqrt{\frac{RT}{M}}$$

$$v_{\text{mp}} = \sqrt{\frac{2k_B T}{m_0}} = 1.41 \sqrt{\frac{k_B T}{m_0}} = 1.41 \sqrt{\frac{RT}{M}}$$

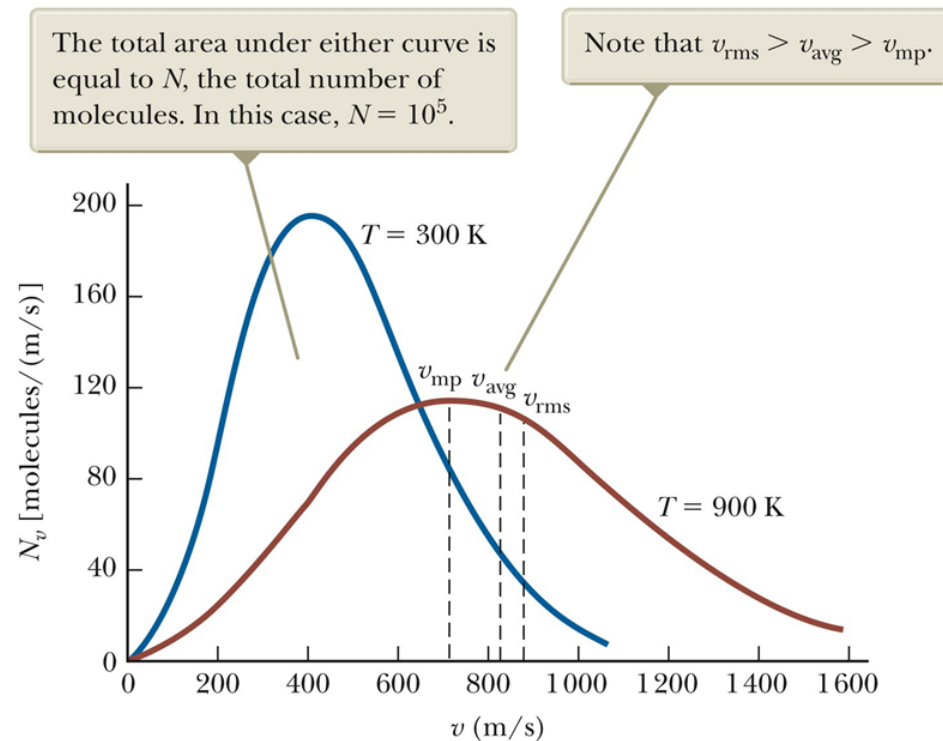
$$v_{\text{rms}} > v_{\text{avg}} > v_{\text{mp}}$$

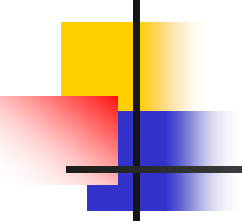
The number of molecules having speeds ranging from v to $v + dv$ equals the area of the tan rectangle, $N_v dv$.



Speed Distribution Curves for Nitrogen, N_2

- The peak shifts to the right as T increases
 - This shows that the average speed increases with increasing temperature
- The asymmetric shape occurs because the lowest possible speed is 0 and the highest is infinity




$$N_v = 4\pi N \left(\frac{m_0}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_0 v^2 / 2k_B T}$$

- The distribution of molecular speeds depends both on the mass and on temperature
- At a given temperature, the fraction of molecules with speeds exceeding a fixed value increases as the mass decreases
 - This explains why lighter molecules (H_2 and He) escape into space from the Earth's atmosphere more easily than heavier molecules
- The speed distribution for liquids is similar to that of gases

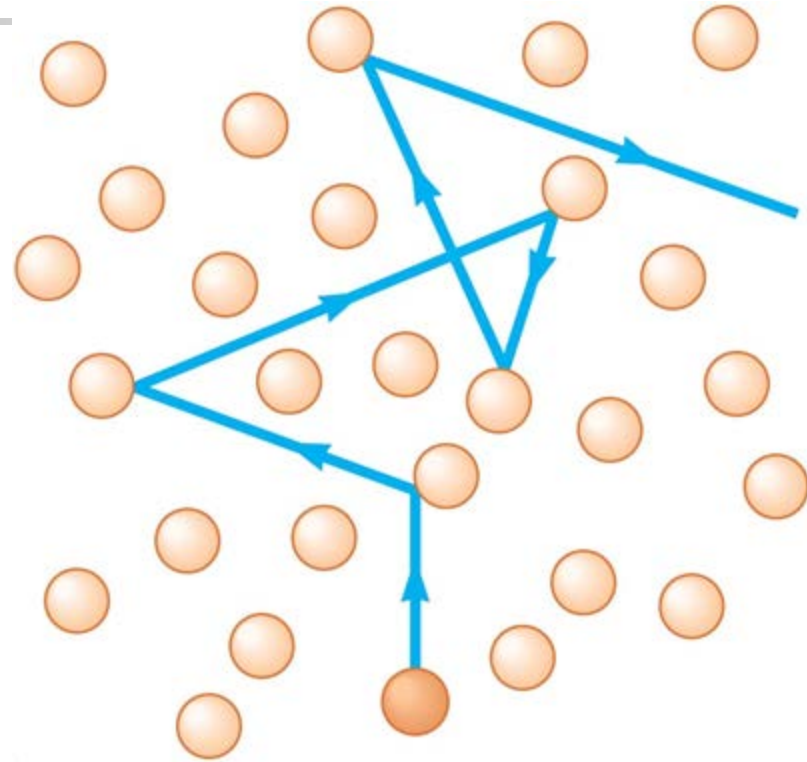


Evaporation

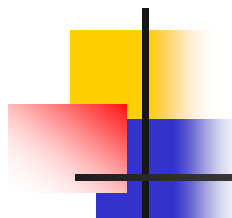
- Some molecules in the liquid are more energetic than others
- Some of the faster moving molecules penetrate the surface and leave the liquid
 - This occurs even before the boiling point is reached
- The molecules that escape are those that have enough energy to overcome the attractive forces of the molecules in the liquid phase
- The molecules left behind have lower kinetic energies
- Therefore, evaporation is a cooling process

Collision between Molecules

- A molecule moving through a gas collides with other molecules in a random fashion
- This behavior is sometimes referred to as a *random-walk process*
- The **mean free path** (the average distance between collisions) increases as the number of molecules per unit volume decreases

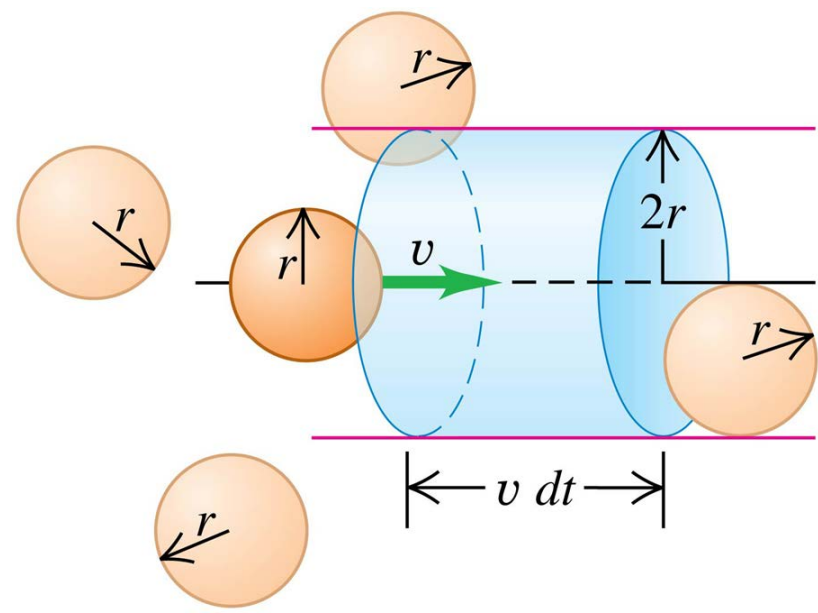


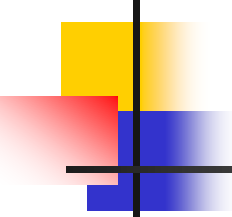
In a time dt a molecule with a radius r will collide with any other molecule within a cylindrical volume of radius $2r$ and length vdt



- When a molecule collides with another molecule, the distance between their centers is $2r$
- The volume of the cylinder is $4\pi r^2 vdt$
- The number of collisions of a molecule with every molecule within the cylinder is $dN = 4\pi r^2 vdt (N/V)$
- The number of collisions *per unit time* is $\frac{dN}{dt} = \frac{4\pi r^2 vN}{V}$
- For all molecules moving at once

$$\frac{dN}{dt} = \frac{4\pi\sqrt{2}r^2vN}{V}$$





$$\frac{dN}{dt} = \frac{4\pi\sqrt{2}r^2vN}{V}$$

- The average time t_{mean} between collisions (*mean free time*) is

$$t_{\text{mean}} = \frac{V}{4\pi\sqrt{2}r^2vN}$$

- Frequency of collisions is $f = 1/t_{\text{mean}} = \frac{4\pi\sqrt{2}r^2vN}{V}$

- The mean free path λ is

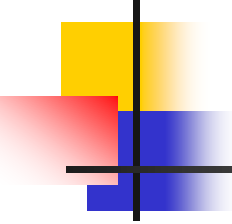
$$\lambda = vt_{\text{mean}} = \frac{V}{4\pi\sqrt{2}r^2N}$$

$$PV = Nk_B T \rightarrow \frac{V}{N} = \frac{k_B T}{P}$$

$$\lambda = \frac{k_B T}{4\pi\sqrt{2}r^2 P}$$

$$f = \frac{4\pi\sqrt{2}r^2 v P}{k_B T}$$

Example: N₂ molecules at 20°C and 1 atm, $r = 1 \times 10^{-10}$ m

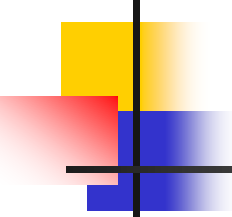


$$\lambda = \frac{k_B T}{4\pi\sqrt{2}r^2 P} = 2.25 \times 10^{-7} \text{ m}$$

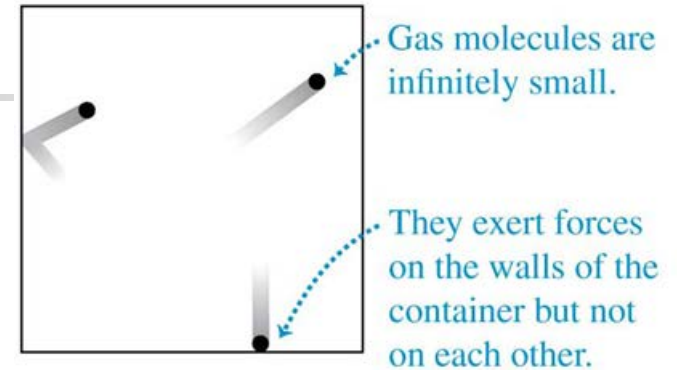
$$v_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} = 471 \text{ m/s}$$

$$f = \frac{4\pi\sqrt{2}r^2 v_{\text{avg}} P}{k_B T} = 2.09 \times 10^9 \text{ s}^{-1}$$

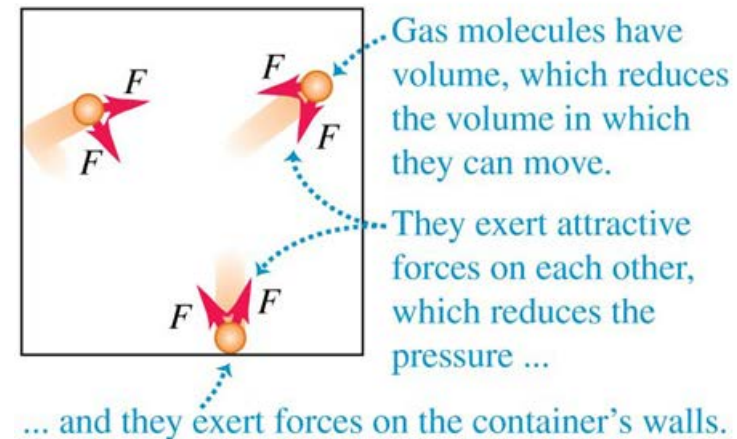
The van der Waals Equation


$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

An idealized model of a gas



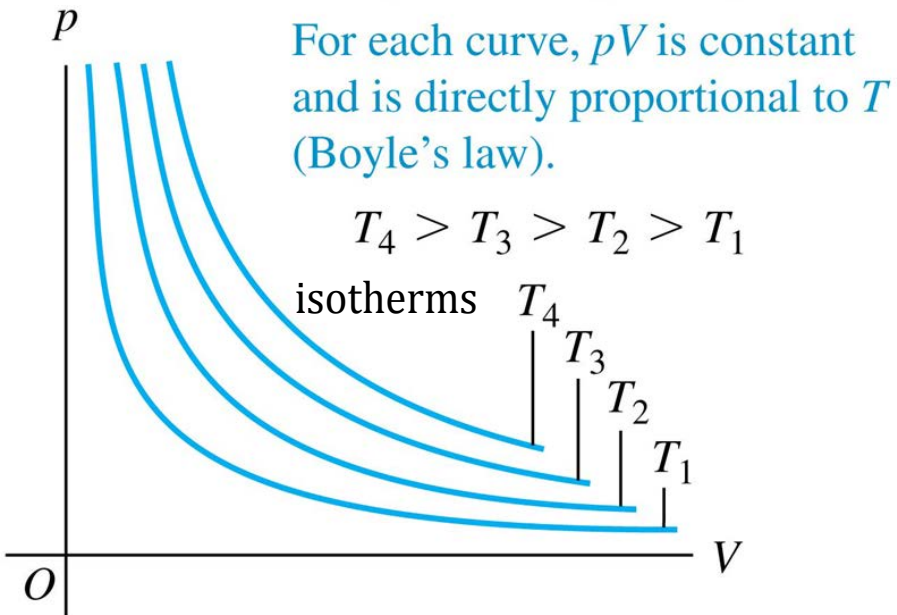
A more realistic model of a gas



- The ideal gas equation ignores 1) the volumes of the molecules and 2) the attractive forces between them
- The van der Waals equation – another equation of state
- a and b are constants (different for different gases)
- CO_2 : $a = 0.364 \text{ J}\cdot\text{m}^3/\text{mol}^2$, $b = 4.27 \times 10^{-5} \text{ m}^3/\text{mol}$

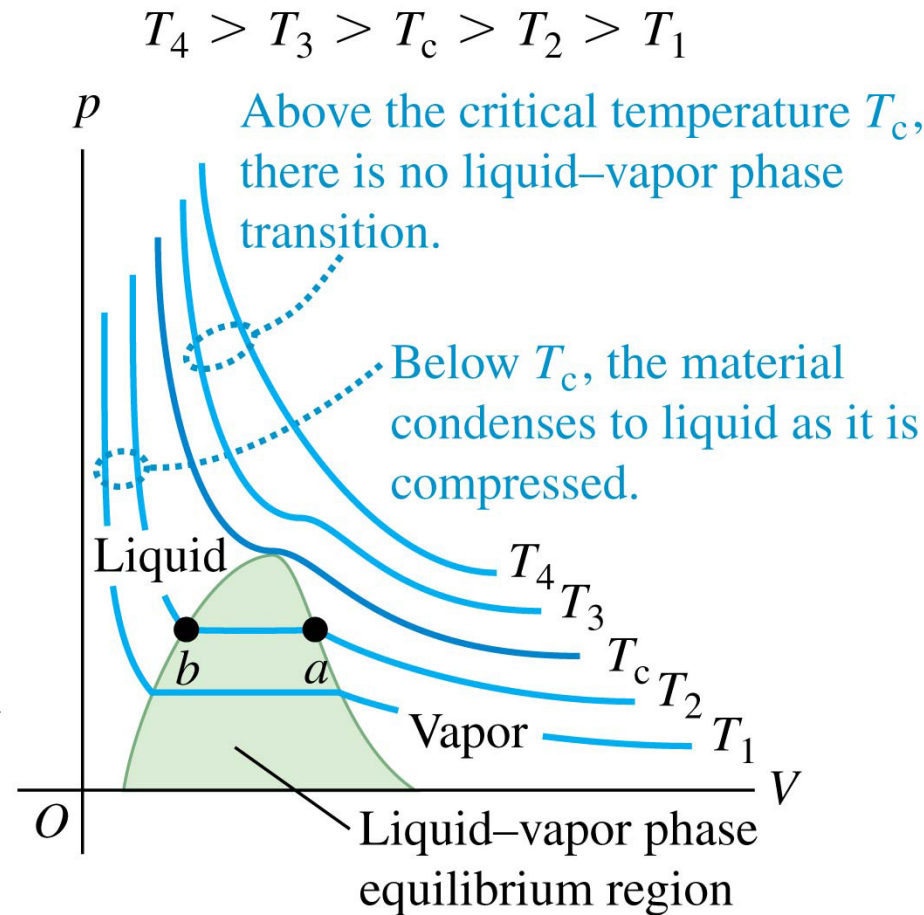
PV Diagrams

Each curve represents pressure as a function of volume for an ideal gas at a single temperature.



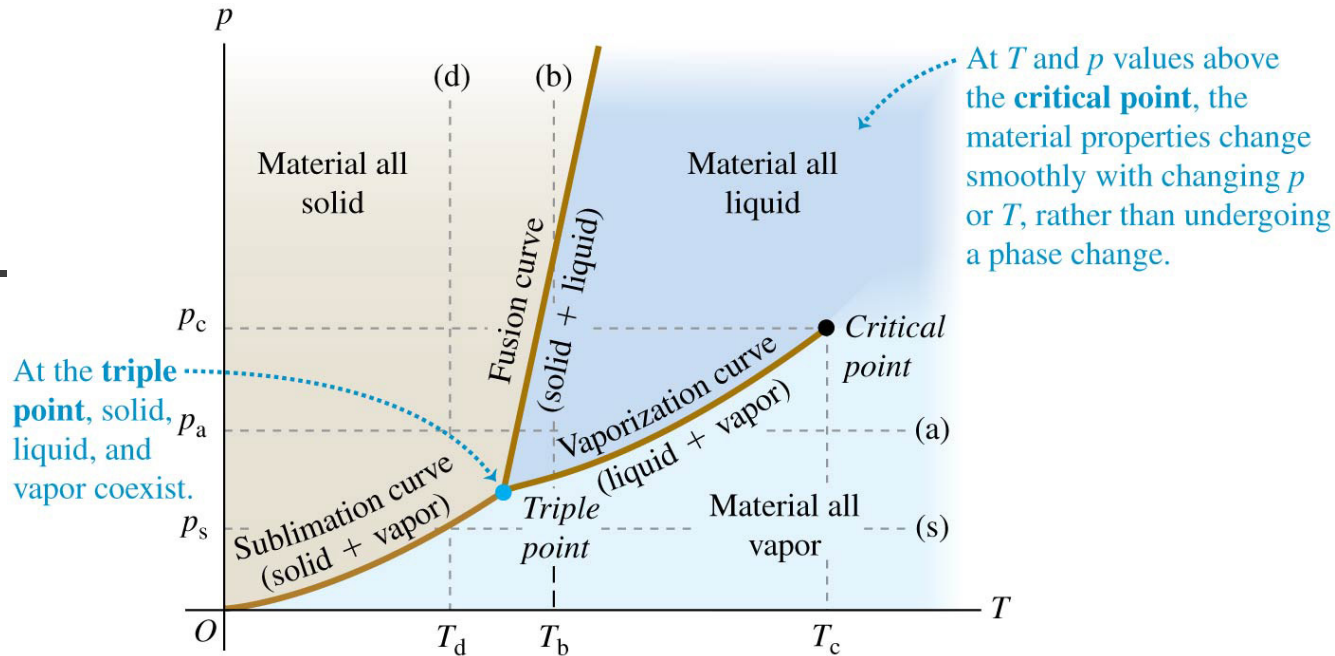
Ideal Gas

- At temperature below T_c (*critical temperature*) the isotherms develop flat regions in which one can compress the material without increasing the pressure $p \rightarrow$
- Compressing a gas at a constant $T_2 \rightarrow$
- At temperature greater than T_c , no phase transition occurs



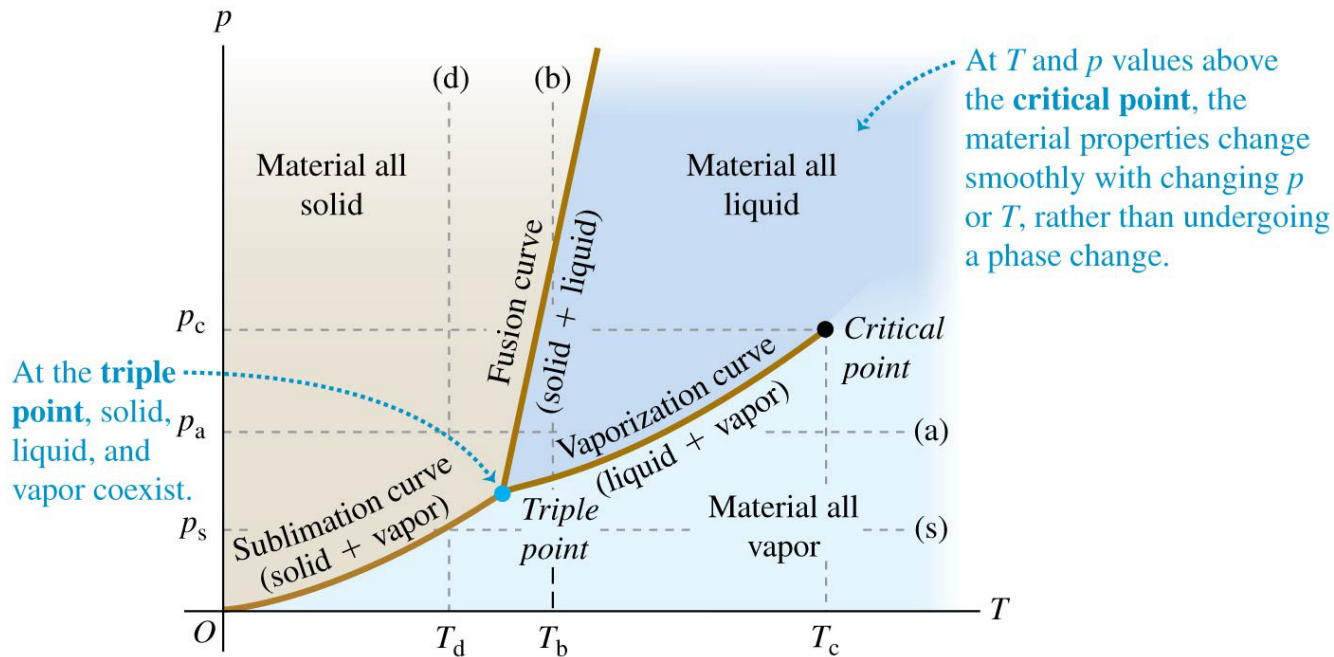
Nonideal Gas

A Phase Diagram $P(T)$



- Only a single phase can exist at each point
- Two phases can coexist in phase equilibrium at the solid lines
- The **fusion**, **vaporization**, and **sublimation** curves; they meet at the **triple point**
- Heating a substance at a constant pressure P_a (melting and boiling) – line (a)
- Heating a substance at a constant pressure P_s (sublimation) – line (s)
- At any pressure less than the triple-point pressure (for CO_2 , 5.1 atm), no liquid phase is possible (at normal atmospheric pressure, “dry ice” = solid CO_2 undergoes sublimation)
- Compression at a constant temperature T_b (vapor \rightarrow liquid \rightarrow solid) – line (b)
- Compression at a constant temperature T_d (vapor \rightarrow solid) – line (d)

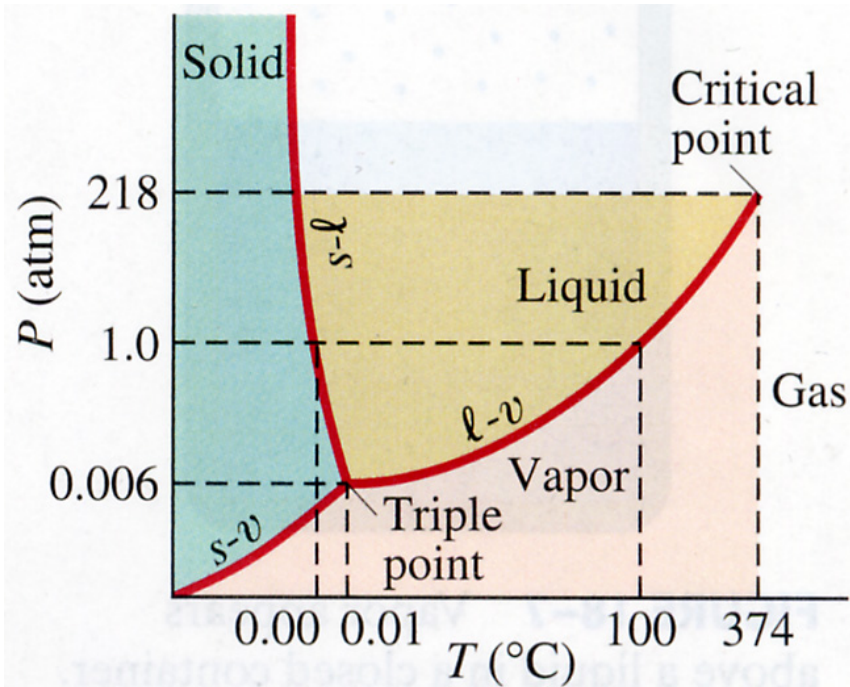
A Phase Diagram $P(T)$



Critical Temperatures and Pressures			
Substance	Critical Temperature		Critical Pressure (atm)
	°C	K	
Water	374	647	218
CO ₂	31	304	72.8
Oxygen	-118	155	50
Nitrogen	-147	126	33.5
Hydrogen	-239.9	33.3	12.8
Helium	-267.9	5.3	2.3

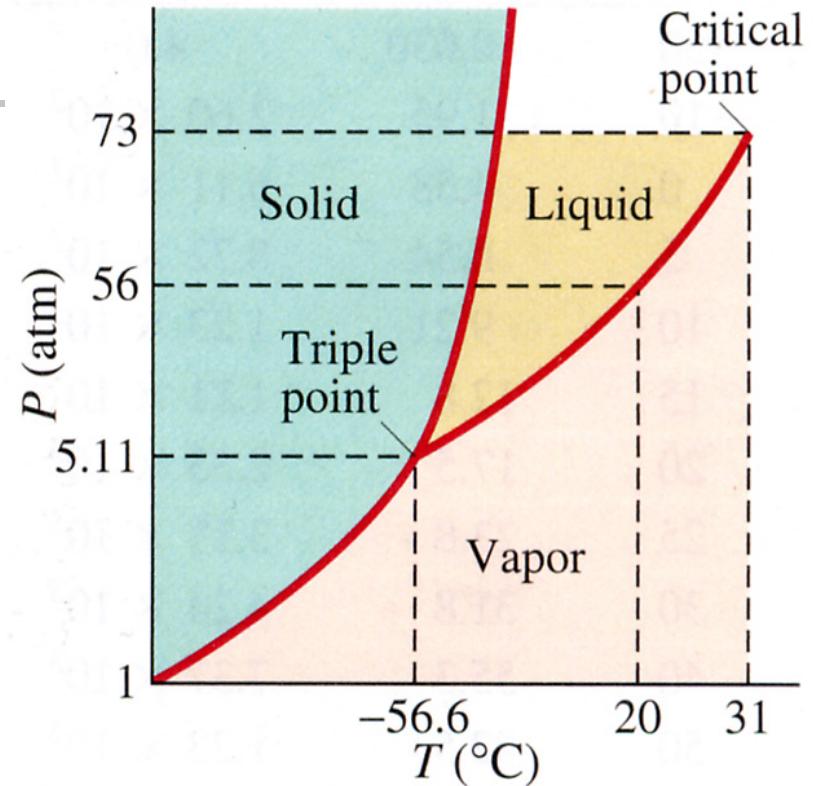
- **Critical point** : critical pressure P_c and critical temperature T_c
- A gas at a pressure $P > P_c$ does not separate into two phases when it is cooled at constant pressure (horizontal line above the critical point). Instead, its properties change gradually and continuously from those associated with a gas (low density, large compressibility) to those associated with a liquid (high density, small compressibility) without a phase transition
- Liquid-phase transitions at successively higher points at the vaporization curve: as one approaches the critical point, the *differences* in physical properties (e.g., density, compressibility, etc.) between the liquid and vapor become smaller. Exactly *at* the critical point they all become zero: the distinction between liquid and vapor disappears; **film 15-11 (CO₂ Critical Point)**

Phase Diagrams (for Water and Carbon Dioxide)

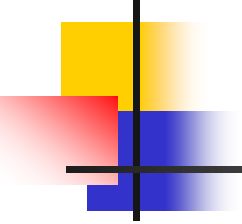


Phase diagram for water (note that the scales are not linear).

Phase diagram for carbon dioxide.



- **Demo:** Regelation
- **Films:** 15-10 (Boiling Water under Reduced Pressure), 15-13 (Freezing by Boiling), 15-16 (Regelation), 15-18 (Sublimation of Carbon Dioxide)



- M1-11, 12