

PHYSICS 2: FLUID MECHANICS AND THERMODYNAMICS

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CHAPTER 3 THE KINETIC THEORY OF GASES

3.1. Ideal Gases

3.2. Mean Free Path

3.3. The Boltzmann Distribution Law and The Distribution of Molecular Speeds

3.4. The Molar Specific Heats of an Ideal Gas

3.5. The Equipartition of Energy Theorem

3.6. The Adiabatic Expansion of an Ideal Gas

3.2. Mean Free Path

3.2.1 Concept

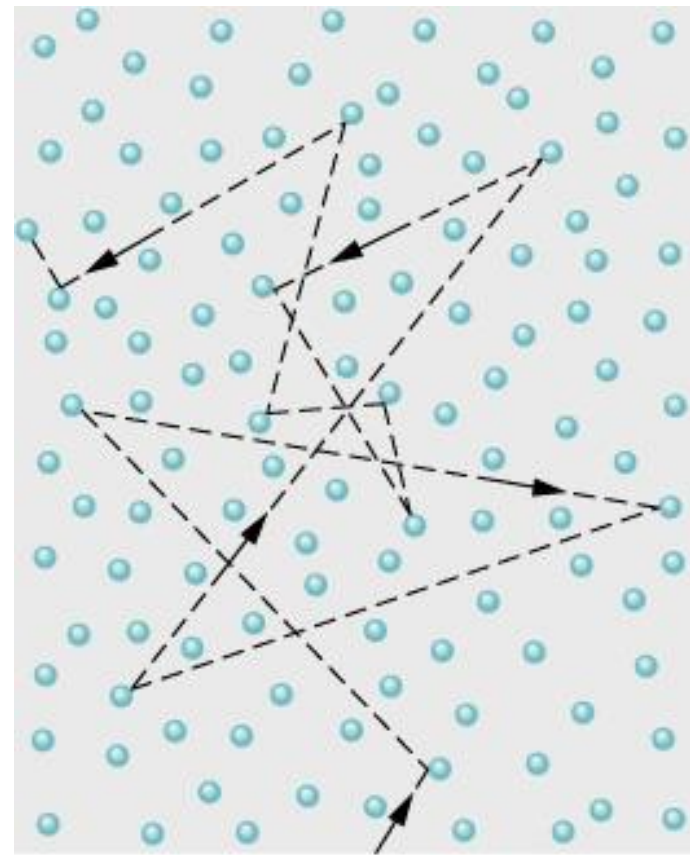
- A molecule traveling through a gas changes both speed and direction as it elastically collides with other molecules in its path.
- Between collisions, the molecules moves in a straight line at constant speed.
- The mean free path λ is the average distance traversed by a molecule between collisions.

$$\lambda \propto \frac{1}{\text{density}} \rightarrow \lambda \propto \frac{1}{\frac{N}{V}}$$

where V is the volume of the gas

N is the number of molecules

$\frac{N}{V}$: the number of molecules per unit volume or the density of molecules



Our goal: Estimate of λ of a single molecule.

Assumptions:

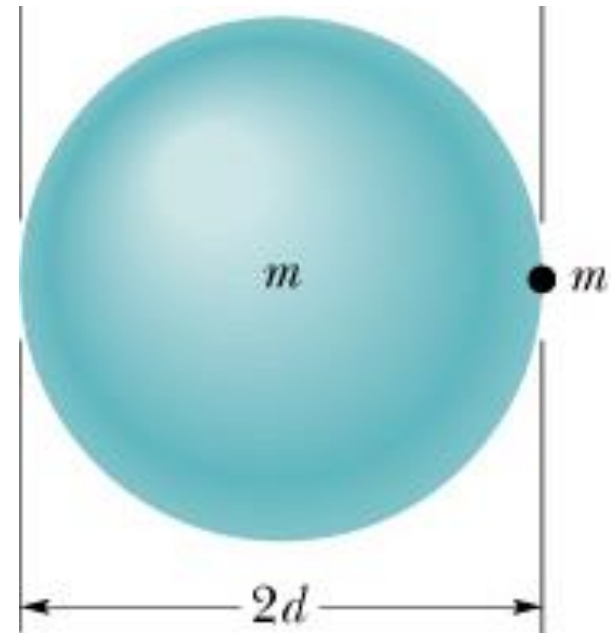
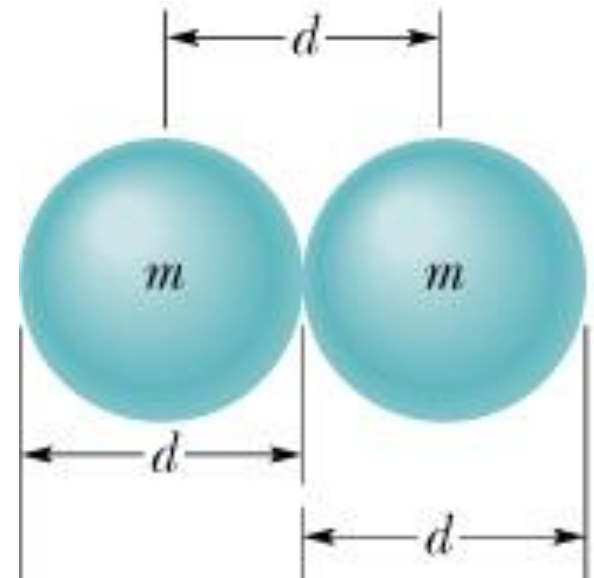
+ Our molecule is traveling with a constant speed v and all the other molecules are at rest.

+ All molecules are spheres of diameter d \rightarrow a collision occurs as the centers of 2 molecules come within a distance d .

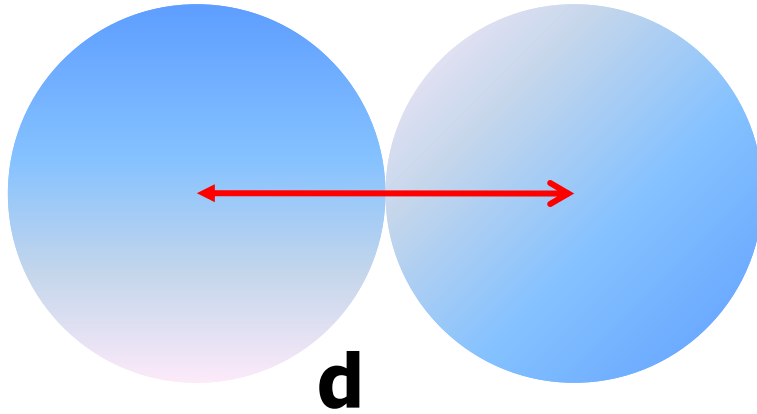
To count the number of collisions:

+ We further consider that this single molecule has an equivalent radius of d and all the other molecules are points.

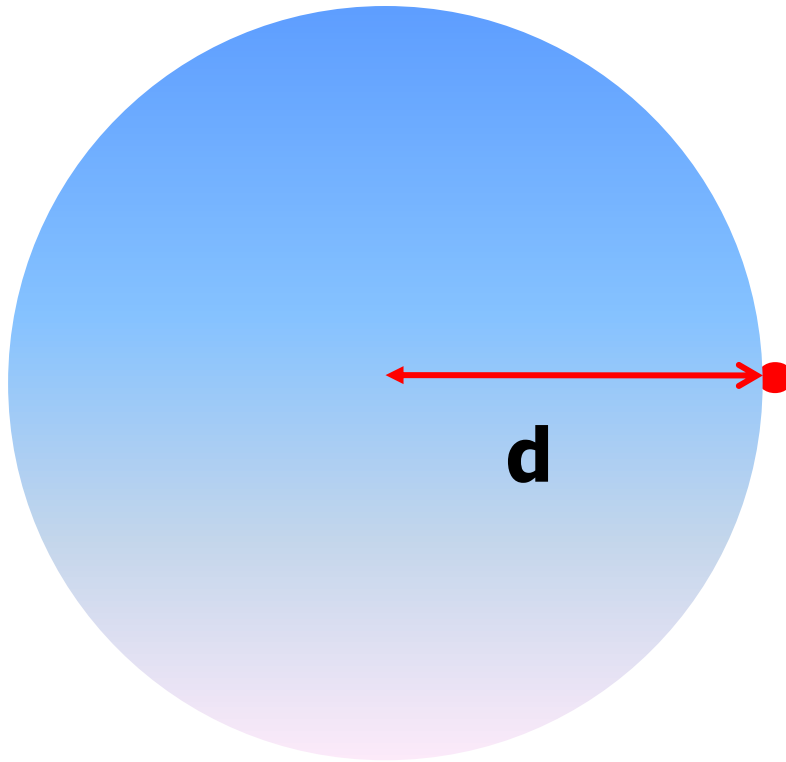
<https://www.youtube.com/watch?v=vUtO3BS-zM>



Equivalent problem

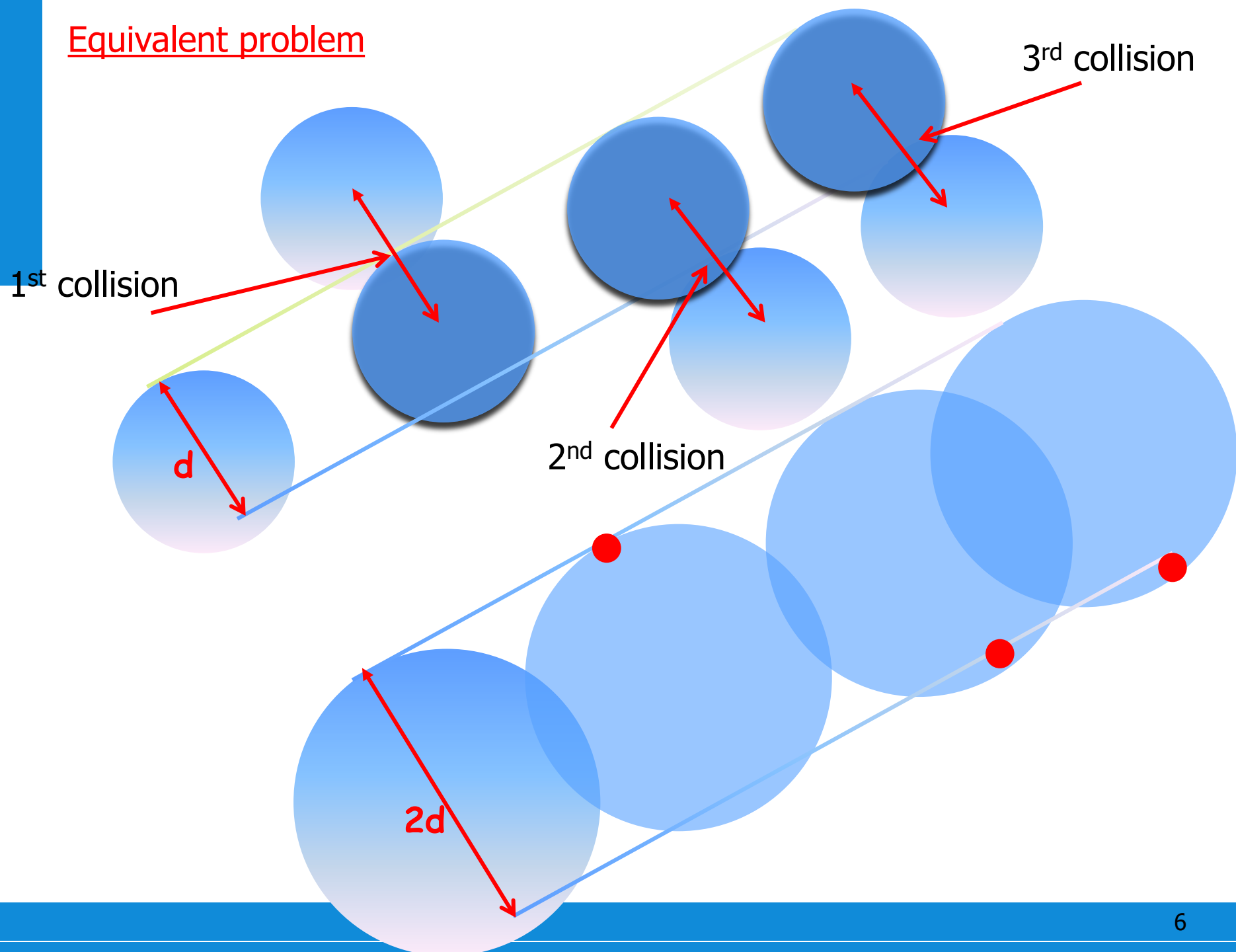


= 1 collision

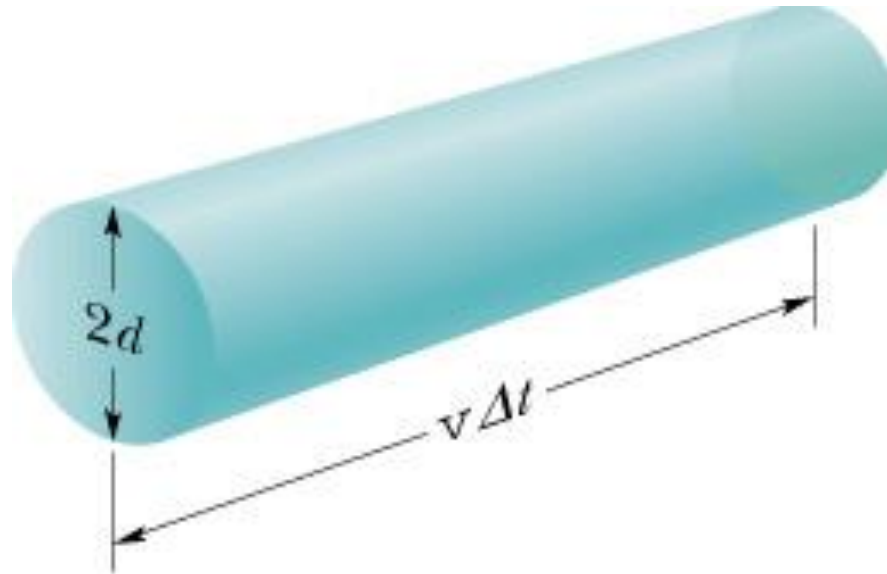


= 1 collision

Equivalent problem



The number of collisions = the number molecules lie in a cylinder of length $v\Delta t$ and cross-sectional area πd^2



$$\lambda = \frac{\text{length of the cylinder of diameter } 2d}{\text{number of molecules}}$$

$$\lambda = \frac{v\Delta t}{V_{\text{cylinder}} \times n} = \frac{v\Delta t}{(\pi d^2 v\Delta t) \times \frac{N}{V}} = \frac{1}{\pi d^2 \frac{N}{V}}$$

If all the molecules are moving:

$$v_{\text{rel}} = \sqrt{2}v_{\text{avg}}$$

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 \frac{N}{V}}$$

Using the equation of state: $pV = NkT$

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 p}$$

The average time between collisions (the mean free time):

$$t = \frac{\lambda}{v} = \frac{kT}{\sqrt{2}\pi d^2 vp}$$

The frequency of collisions:

$$f = \frac{1}{t}$$

Problem 28. At what frequency would the wavelength of sound in air be equal to the mean free path of oxygen molecules at 1.0 atm pressure and 0.0°C? take the diameter of an oxygen molecule to be 3.0×10^{-8} cm.

Frequency of sound in air: $f_{\text{sound}} = \frac{v_{\text{sound in air}}}{\lambda_{\text{sound}}} = \frac{v_{\text{sound in air}}}{\lambda_{\text{MFP}}}$

Mean Free Path: $\lambda_{\text{MFP}} = \frac{kT}{\sqrt{2}\pi d^2 p}$

$$k = 1.38 \times 10^{-23} \text{ J/K}; \quad T = 273 \text{ K}; \quad p = 1.01 \times 10^5 \text{ Pa};$$

$$d = 3 \times 10^{-8} \text{ cm} = 3 \times 10^{-10} \text{ m}$$

$$\rightarrow \lambda_{\text{MFP}} = 9.33 \times 10^{-8} \text{ m}$$

$$v_{\text{sound in air}} = 331 \text{ (m/s)}$$

At 0°C (Table 17.1 in Textbook)

$$\rightarrow f_{\text{sound}} = \frac{331}{9.33 \times 10^{-8}} = 3.5 \times 10^9 \text{ (Hz) or } 3.5 \text{ GHz}$$

3.3. The Boltzmann Distribution Law and the Distribution of Molecular Speeds

The Boltzmann distribution law states that if the energy is associated with some state or condition of a system is ϵ then the frequency with which that state or condition occurs, or the probability of its occurrence is proportional to:

$$e^{-\epsilon / kT}$$

k : the Boltzmann constant

Many of the most familiar laws of physical chemistry are special cases of the Boltzmann distribution law:

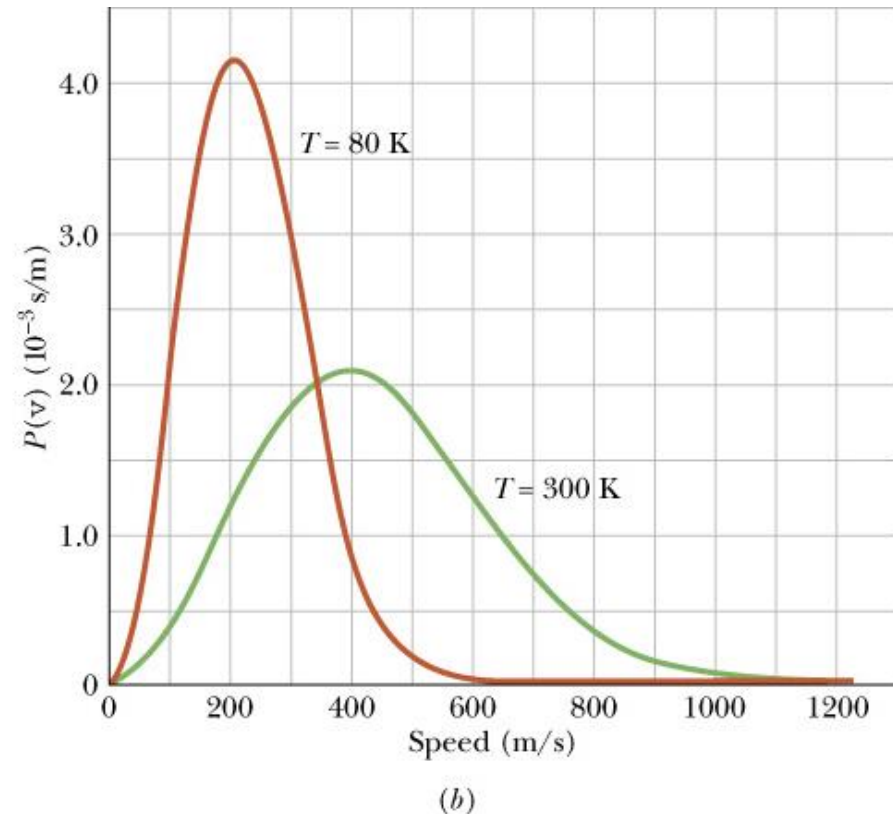
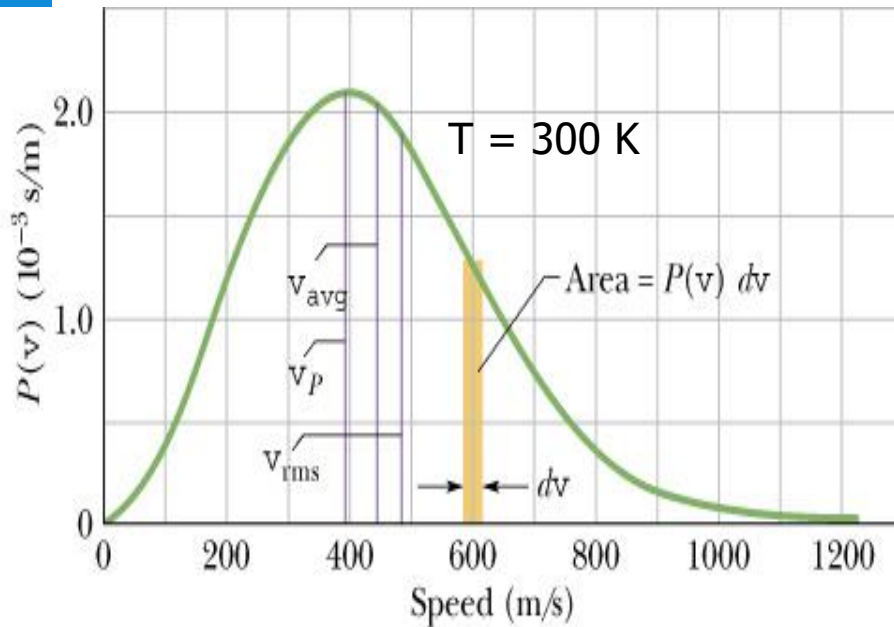
3.3.1. The distribution of molecular speeds (or the Maxwell speed distribution law):

- Let M be the molar mass of the gas, v be the molecular speed, and $P(v)$ be the speed distribution function:

$$P(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2 / 2kT} \quad (1)$$

Probability distribution function:

$P(v)dv$ is the fraction of molecules with speeds in the infinitesimal range $(v, v+dv)$.



$$\int_0^{\infty} P(v) dv = 1$$

The fraction of molecules with speeds from v_1 to v_2 :

$$\text{frac} = \int_{v_1}^{v_2} P(v) dv$$

Average, RMS, and Most Probable Speeds

The average speed:

$$\bar{v} = \int_0^{\infty} v P(v) dv \quad (2)$$

from (1) & (2):

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

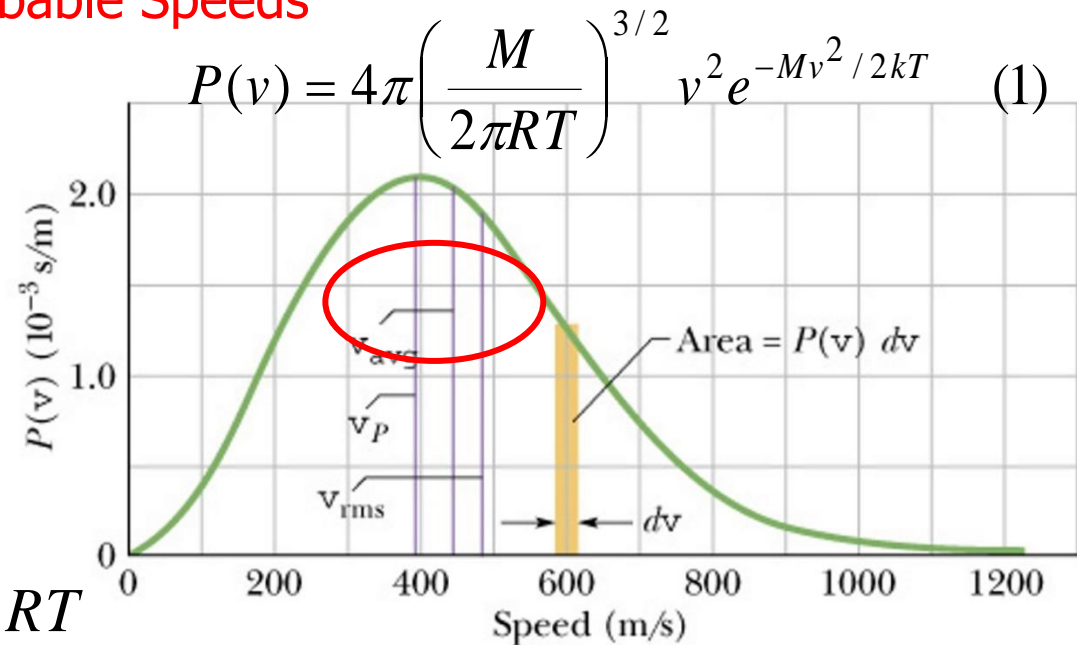
$$\overline{v^2} = \int_0^{\infty} v^2 P(v) dv \quad \overline{v^2} = \frac{3RT}{M}$$

The root-mean-square speed:

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

The most probable speed is the speed at which $P(v)$ is maximum:

$$\frac{dP(v)}{dv} = 0 \quad v_P = \sqrt{\frac{2RT}{M}}$$



Problem 33. The speeds of 10 molecules are 2.0, 3.0, 4.0,..., 11 km/s. What are their (a) average speed and (b) rms speed?

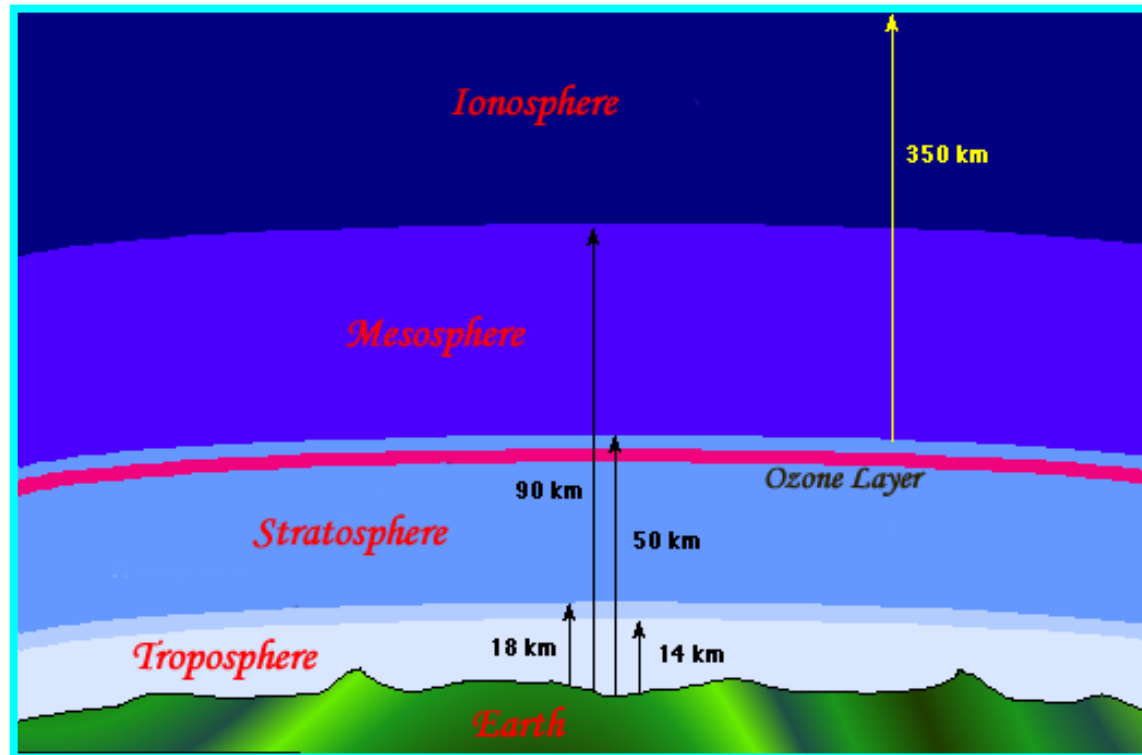
$$(a) \quad \bar{v} = \frac{\sum_{i=1}^N v_i}{N} = \frac{2+3+4+\dots+11}{10} = \frac{65}{10} = 6.5 \text{ (km/s)}$$

$$(b) \quad v_{rms} = \sqrt{(v^2)_{avg}} = \sqrt{\frac{\sum_{i=1}^N v_i^2}{N}} = 7.1 \text{ (km/s)}$$

3.3.2. The barometric distribution law:

This law gives the number density $\rho(h)$, i.e. number of molecules per unit volume, of an ideal gas of uniform temperature T as a function of height h in the field of the Earth's gravity. Where, h_0 is an arbitrary fixed reference height; m is the mass of a molecule.

$$\rho(h) = \rho(h_0) e^{-mg(h-h_0)/kT}$$



(nasa.gov)

Chapter 3 The Kinetic Theory of Gases

3.1. Ideal Gases

3.1.1. Experimental Laws and the Equation of State

3.1.2. Molecular Model of an Ideal Gas

3.2. Mean Free Path

3.3. The Boltzmann Distribution Law and The Distribution of Molecular Speeds

3.4. The Molar Specific Heats of an Ideal Gas

3.5. The Equipartition of Energy Theorem

3.6. The Adiabatic Expansion of an Ideal Gas

3.4. The Molar Specific Heats of an Ideal Gas

Let's consider our ideal gas of n moles that is a monatomic gas, which has individual atoms, e.g. helium, argon, neon. For a single atom, the average translational KE:

$$\overline{K} = \frac{3}{2} kT$$

The internal energy E_{int} of the gas (no rotational KE for monatomic gases):

$$E_{\text{int}} = \sum_1^N \overline{K} = \frac{3}{2} kT \times nN_A = \frac{3}{2} nRT$$

$$\Delta E_{\text{int}} = \frac{3}{2} nR\Delta T$$

Recall molar specific heat:

$$Q = Cn\Delta T$$

Problem 25. Determine the average value of the translational kinetic energy of the molecules of an ideal gas at (a) 0°C and (b) 100°C. What is the translational kinetic energy per mole of an ideal gas at (c) 0°C and (d) 100°C?

(a) The translational kinetic energy per molecule: $\overline{K} = \frac{3}{2} kT$

$$T = 0 + 273 = 273 \text{ K}:$$

$$\overline{K} = \frac{3}{2} \times 1.38 \times 10^{-23} \times 273 = 5.65 \times 10^{-21} \text{ (J)}$$

(b) similarly: $\overline{K} = \frac{3}{2} \times 1.38 \times 10^{-23} \times 373 = 7.72 \times 10^{-21} \text{ (J)}$

(c) The translational kinetic energy per mole: $K_{mole} = \overline{K} \times N_A$

$$K_{mole} = 5.65 \times 10^{-21} \times 6.02 \times 10^{23} = 3.4 \times 10^3 \text{ (J)}$$

(d) $K_{mole} = 4.7 \times 10^3 \text{ (J)}$

Note: If a sample of gas has n moles (or N molecules), its total translational kinetic energy is:

$$K_{total} = n \times K_{mole} = n \times N_A \times \overline{K}$$

$$K_{total} = n \times K_{mole} = n \times N_A \times \frac{3}{2} kT = \frac{3}{2} nRT$$

$$K_{total} = \frac{3}{2} nRT$$

a. Molar specific heat at constant volume:

- Consider n moles of an ideal gas at state i : p , T , and fixed $V \rightarrow$ state f : $p + \Delta p$, $T + \Delta T$

$$Q = nC_V \Delta T$$

C_V is a constant and called the molar specific heat at constant volume.

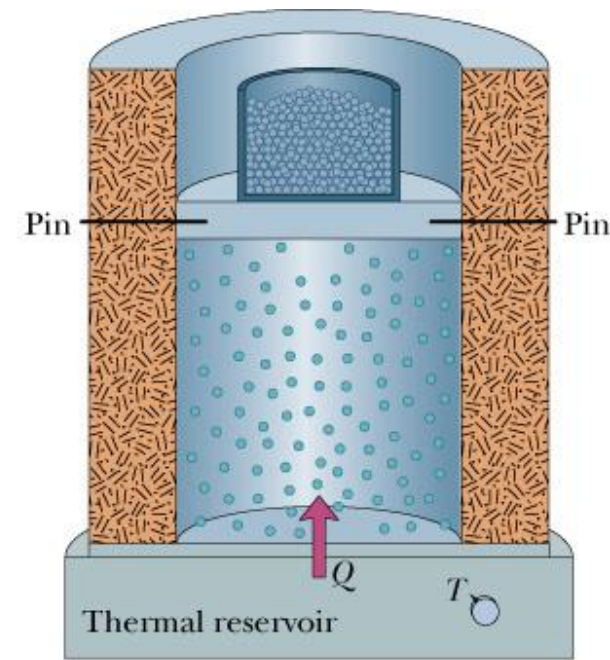
$$\Delta E_{\text{int}} = Q - W = nC_V \Delta T - W = \frac{3}{2} nR \Delta T$$

$$\text{Since } W = 0, C_V = \frac{3}{2} R = 12.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

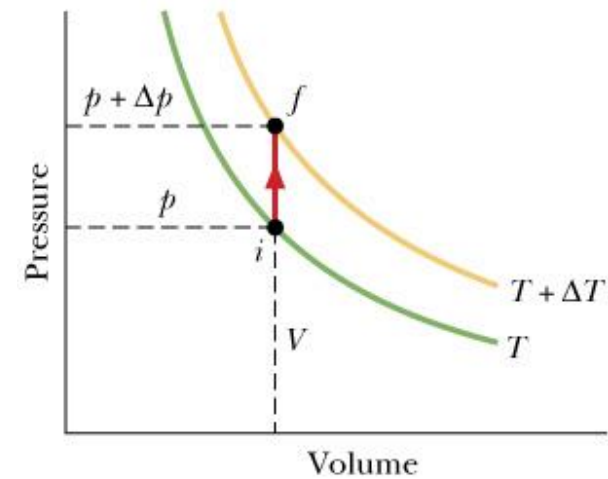
Note: For diatomic and polyatomic gases, their C_V is greater than that of monatomic gases.

So, the change in internal energy can be calculated by:

$$\Delta E_{\text{int}} = \frac{3}{2} nR \Delta T \quad \text{or} \quad \Delta E_{\text{int}} = nC_V \Delta T$$



(a)



(b)

b. Molar specific heat at constant pressure:

$$Q = nC_p\Delta T$$

C_p is the molar specific heat at constant pressure.

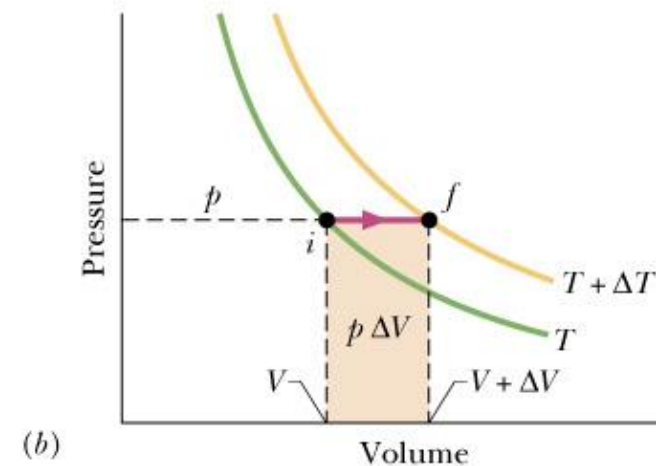
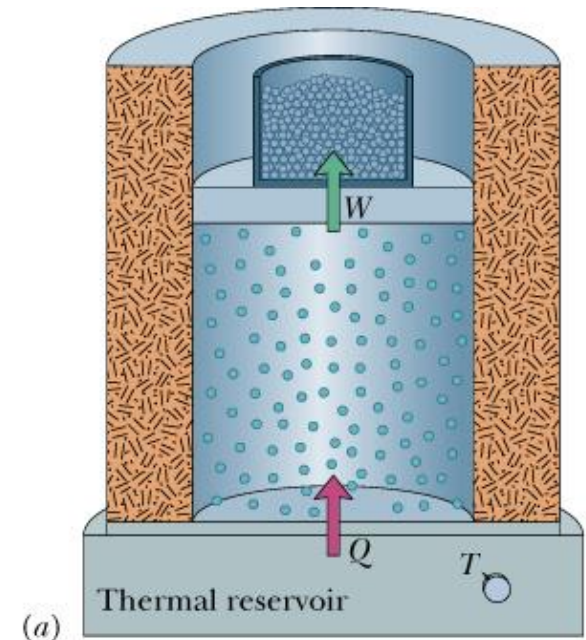
$$\Delta E_{\text{int}} = Q - W$$

$$W = p\Delta V = nR\Delta T$$

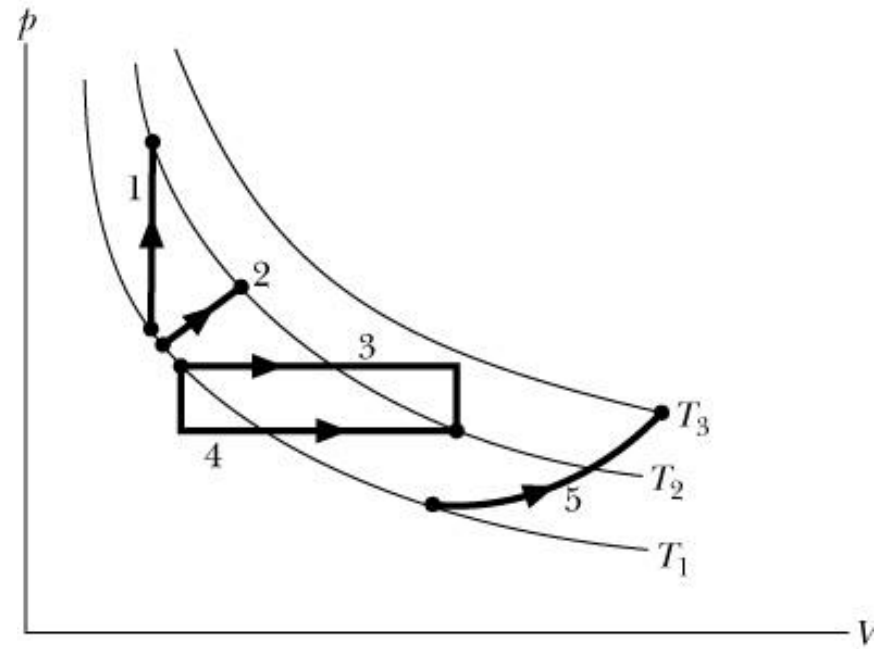
$$\Rightarrow \frac{3}{2}nR\Delta T = nC_p\Delta T - nR\Delta T$$

$$C_p = \frac{3}{2}R + R = \frac{5}{2}R$$

$$C_p = C_V + R$$



Checkpoint: The figure here shows 5 paths traversed by a gas on a p-V diagram. Rank the paths according to the change in internal energy of the gas, greatest first.



Problem 8. Suppose 1.8 mol of an ideal gas is taken from a volume of 3.0 m³ to a volume of 1.5 m³ via an isothermal compression at 30°C. (a) How much energy is transferred as heat during the compression, and (b) is the transfer to or from the gas?

(a) We have: $\Delta E_{\text{int}} = Q - W$

An isothermal process: $T = \text{constant}$

$$\Delta E_{\text{int}} = 0 \Rightarrow Q = W$$

Work done by the gas for isotherm:

$$W = nRT \ln \frac{V_f}{V_i}$$

$$Q = W = 1.8 \times 8.31 \times (30 + 273) \times \ln \frac{1.5}{3.0} \approx -3142 \text{ (J)}$$

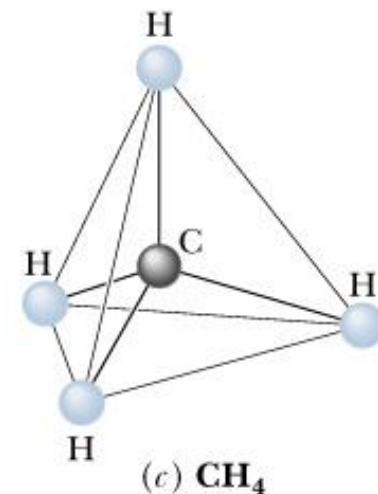
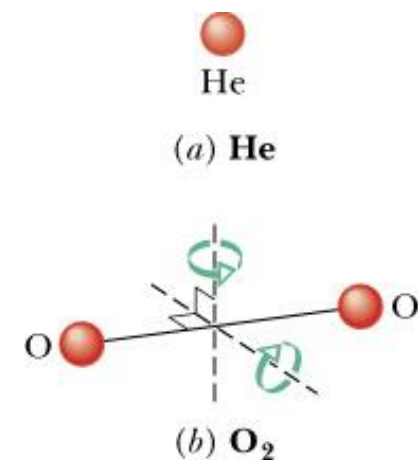
(b) $Q < 0$: heat transferred from the gas

3.5. The Equipartition-of-Energy Theorem

Every kind of molecule has a certain number f of *degrees of freedom*. For each degree of freedom in which a molecule can store energy, the average internal energy is $\frac{1}{2}kT$ per molecule.

$$C_V = \left(\frac{f}{2}\right)R$$

$$C_p = C_V + R$$



Molecule	Example	Degrees of freedom		
		Translational	Rotational	Total (f)
Monatomic	He	3	0	3
Diatomic	O ₂	3	2	5
Polyatomic	CH ₄	3	3	6

3.6. The Adiabatic Expansion of an Ideal Gas

What is an adiabatic process? a process for which $Q = 0$

$$pV^\gamma = \text{constant}$$

where $\gamma = C_p/C_v$ $pV = nRT$

Equation of state:

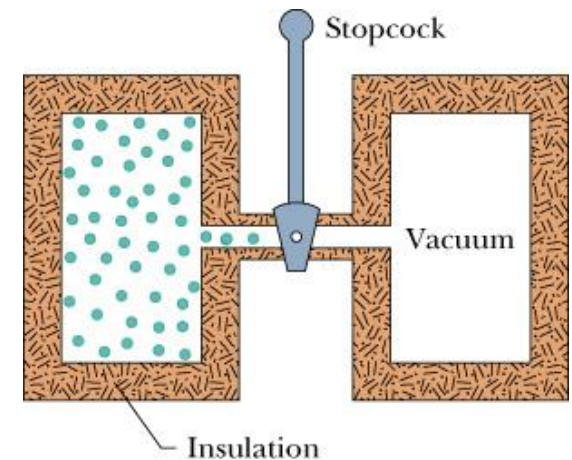
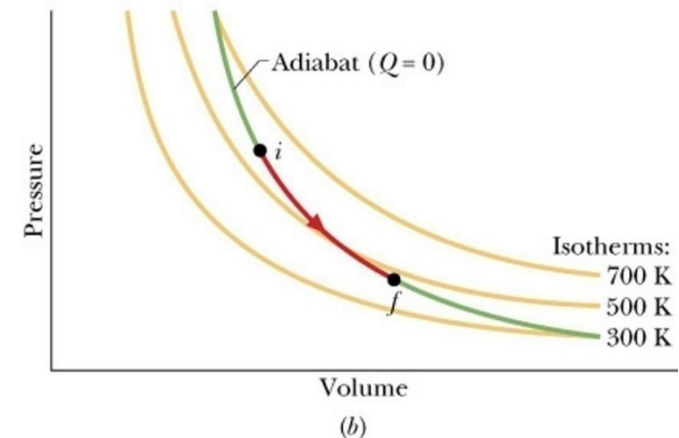
$$TV^{\gamma-1} = \text{constant}$$

Free expansions:

Recall: $Q = W = 0$

$$\Delta E_{\text{int}} = 0 \Rightarrow T_i = T_f$$

$$p_i V_i = p_f V_f$$



Homework: 32, 33, 40, 42, 44, 46, 54, 56, 78 – Chapter 19 in Textbook