

**Homework: 13, 14, 18, 20, 24 (p. 531-532)**

13. A sample of an ideal gas is taken through the cyclic process abca shown in the figure below; at point a,  $T=200$  K. (a) How many moles of gas are in the sample? What are (b) the temperature of the gas at point b, (c) the temperature of the gas at point c, and (d) the net energy added to the gas as heat during the cycle?

(a) Applying the equation of state:

$$pV = nRT \Rightarrow n = \frac{pV}{RT}$$

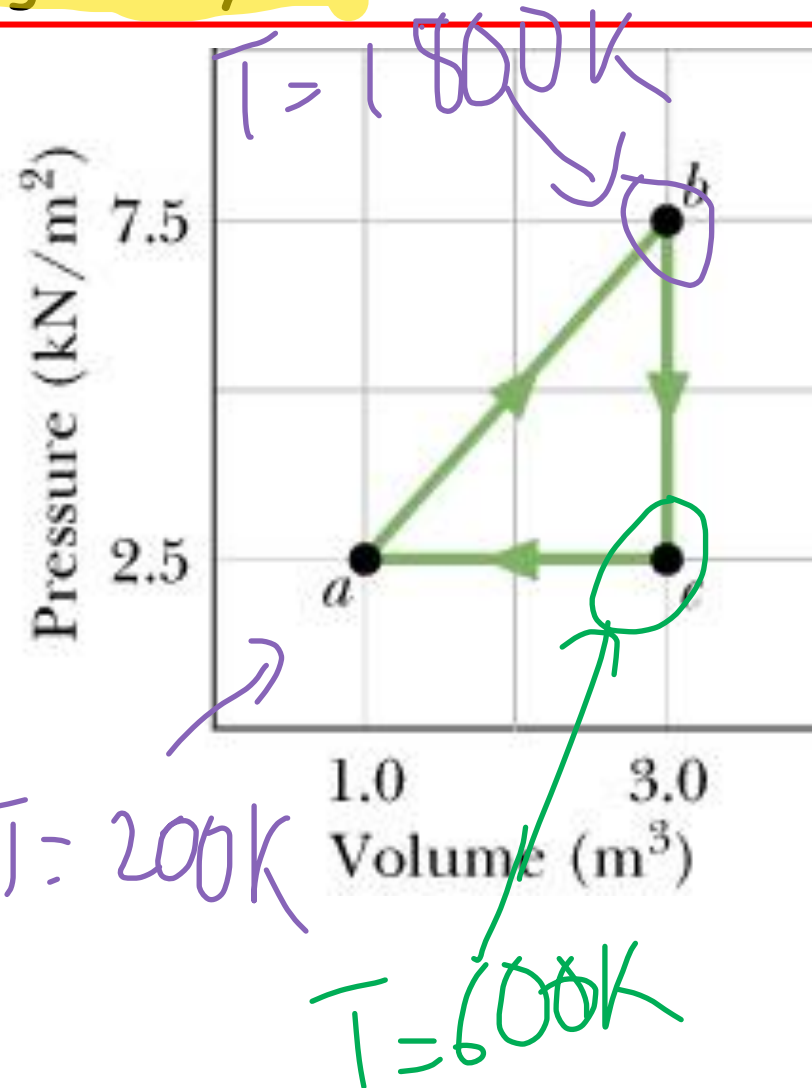
At point a,  $p=2.5$  kN/m<sup>2</sup> or 2500 N/m<sup>2</sup>;  
 $V=1$  m<sup>3</sup>.

$$n = \frac{2500 \times 1}{8.31 \times 200} = 1.5 \text{ (mol)}$$

(b)  $pV = nRT \Rightarrow \frac{p_a V_a}{T_a} = \frac{p_b V_b}{T_b} = nR = 12.5$

At point b,  $p=7.5$  kN/m<sup>2</sup> or 7500 N/m<sup>2</sup>;  
 $V=3$  m<sup>3</sup>.

$$T_b = \frac{p_b V_b}{nR} = \frac{7500 \times 3}{12.5} = 1800 \text{ (K)}$$



(c) see part b;  $T_c = 600 \text{ K}$ ;  $\frac{p_c V_c}{nR} =$

(d) Applying the first law of thermodynamics:

$$\Delta E = Q - W$$

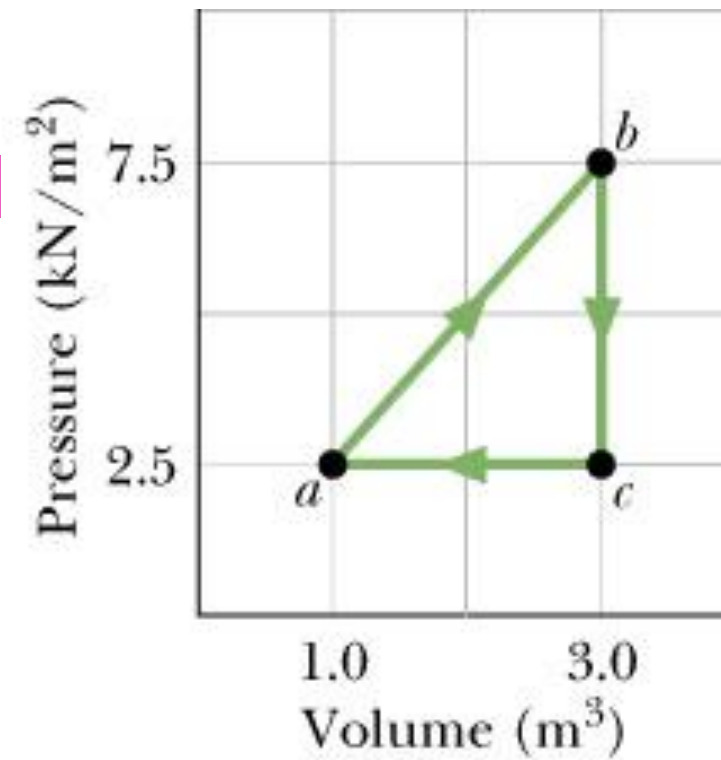
$W$ : work done by the system.

For a closed cycle,  $\Delta E = 0$ :

$$Q = W =$$

$$W = \frac{1}{2} (p_b - p_c) (V_b - V_a)$$

$$W = \frac{1}{2} \times 5000.0 \times 2 = 5 \times 10^3 \text{ (J)}$$



**14.** In the temperature range 310 K to 330 K, the pressure  $p$  of a certain nonideal gas is related to volume  $V$  and temperature  $T$  by:

$$p = (24.9 \text{ J / K}) \frac{T}{V} - (0.00662 \text{ J / K}^2) \frac{T^2}{V}$$

How much work is done by the gas if its temperature is raised from 315 K to 330 K while the pressure is held constant?

• Work done by the gas is computed by the following formula:

$$W = \int_{V_i}^{V_f} p dV = p(V_f - V_i)$$

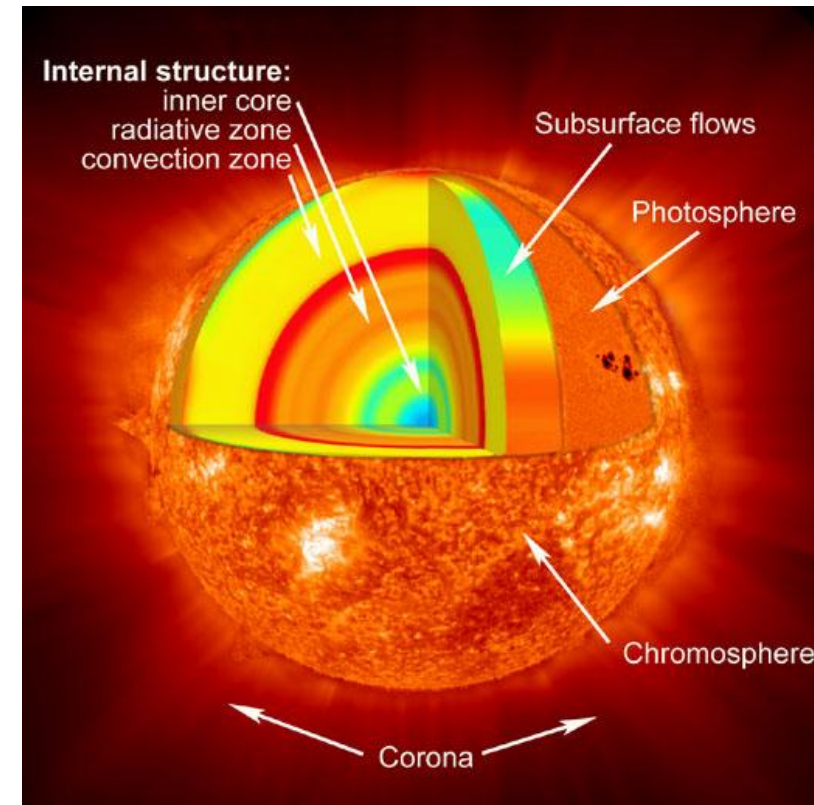
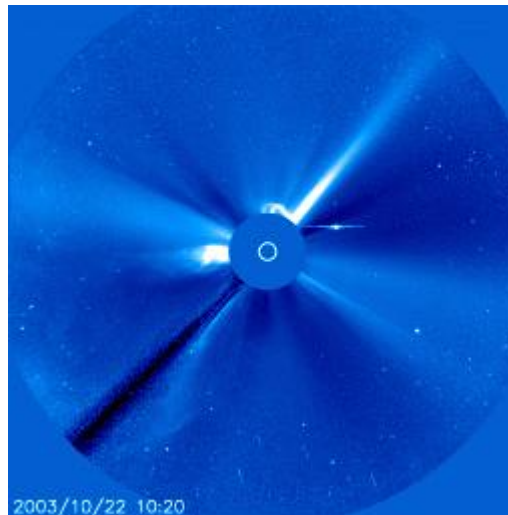
$$W = pV_f - pV_i = 24.9(T_f - T_i) - 0.00662(T_f^2 - T_i^2)$$

$$T_f = 330\text{K}; T_i = 315\text{K} \Rightarrow W \approx 310\text{(J)}$$

18. The temperature and pressure in the Sun's atmosphere are  $2.00 \times 10^6$  K and 0.0300 Pa. Calculate the rms speed of free electrons (mass  $9.11 \times 10^{-31}$  kg) there, assuming they are an ideal gas.

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3RT}{mN_A}}$$
$$v_{rms} = \sqrt{\frac{3 \times 8.31 \times 2 \times 10^6}{9.11 \times 10^{-31} \times 6.023 \times 10^{23}}} = 9.5 \times 10^6 \text{ (m/s)}$$

$$M = m N_A$$



20. Calculate the rms speed of helium atoms at 1000 K, the molar mass of helium atoms is 4.0026 g/mol.

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 1000}{4.0026 \times 10^{-3}}} = 2.5 \times 10^3 \text{ (m/s)}$$

$$m N_A = M = \frac{m}{n}$$



molar  
mass

24. At 273 K and  $1.0 \times 10^{-2}$  atm, the density of a gas is  $1.24 \times 10^{-5}$  g/cm<sup>3</sup>. (a) Find  $v_{rms}$  for the gas molecules. (b) Find the molar mass of the gas and (c) identify the gas (hint: see Table 19-1).

(a) Root-mean-square speed: 
$$v_{rms} = \sqrt{\frac{3RT}{M}} \quad (1)$$

$$\rho = \frac{M_{gas}}{V} = \frac{nM}{V} \Rightarrow M = \frac{\rho V}{n} \quad (2)$$

(1) and (2): 
$$v_{rms} = \sqrt{\frac{3nRT}{\rho V}} = \sqrt{\frac{3p}{\rho}}$$
  $pV = nRT$

$$\rho = 1.24 \times 10^{-5} \text{ g/cm}^3 = 1.24 \times 10^{-2} \text{ kg/m}^3$$

$$p = 1.0 \times 10^{-2} \text{ atm} = 1.01 \times 10^3 \text{ Pa}$$

$$v_{rms} \approx 494 \text{ m/s}$$

(b)

$$M = \frac{\rho V}{n} \quad (2)$$

Equation of state:

$$pV = nRT \quad (3)$$

$$M = \rho \frac{nRT}{np} \\ = \rho \frac{RT}{p}$$

$$\Rightarrow M = \frac{\rho V}{n} = \frac{\rho RT}{p}$$

$$\Rightarrow M \approx 0.028 \text{ kg/mol} = 28 \text{ g/mol}$$

(c)

From Table 19.1, the gas is **nitrogen ( $\text{N}_2$ )**



# 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

## 3.2. Mean Free Path

### 3.2.1 Concept

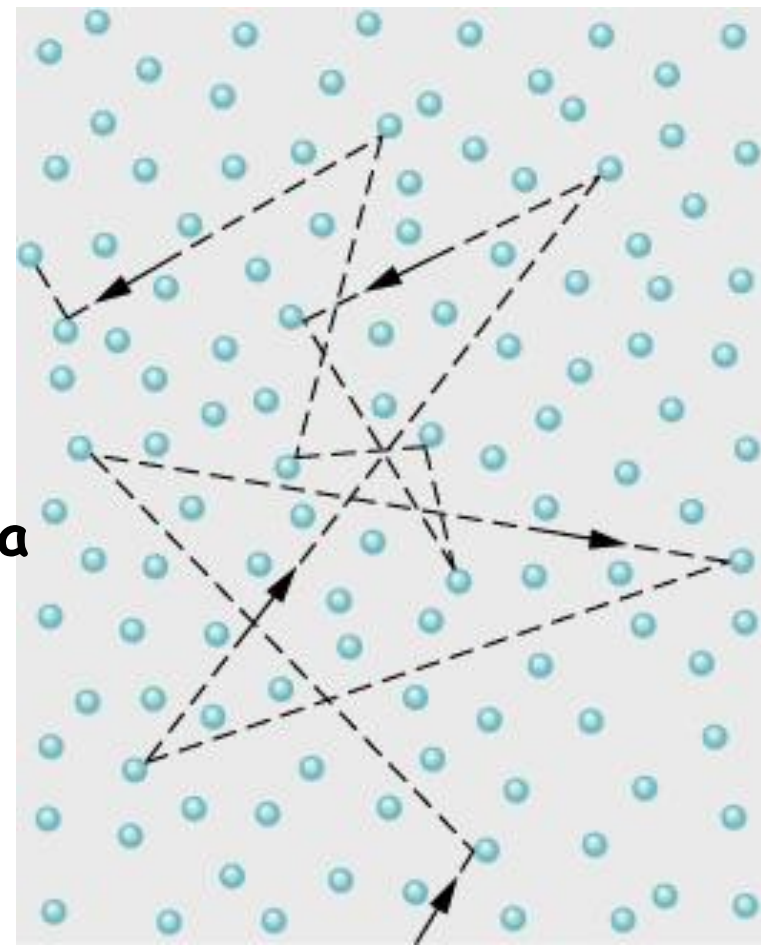
- A molecule traveling through a gas changes both speed and direction as it elastically collides with other molecules in its path.
- Between collisions, the molecules moves in a straight line at constant speed.
- The mean free path  $\lambda$  is the average distance traversed by a molecule between collisions.

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

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



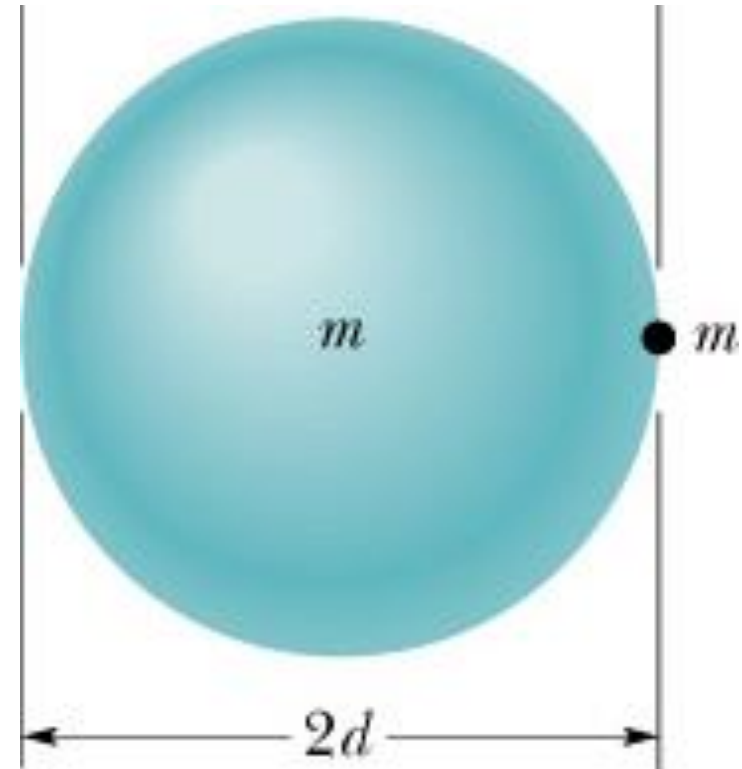
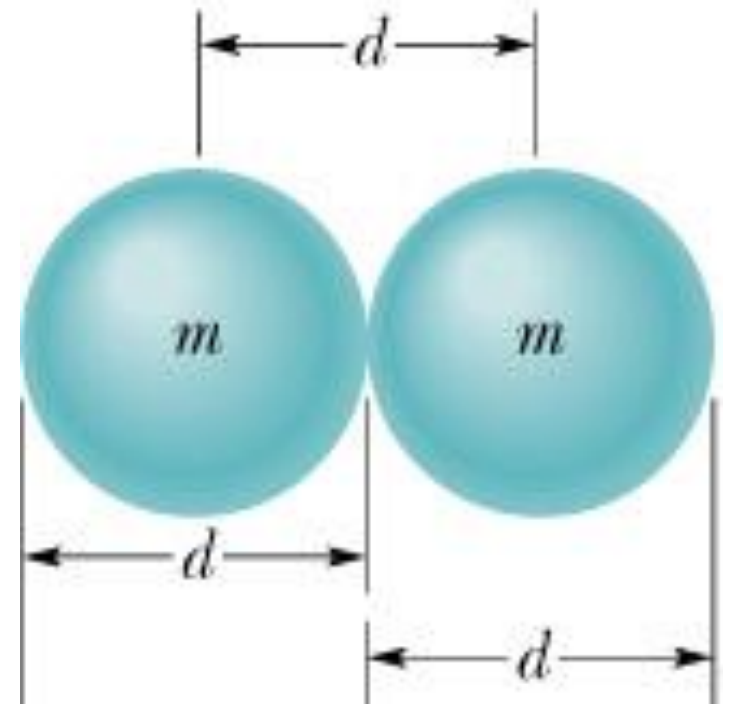
Our goal: Estimate of  $\lambda$  of a single molecule.

Assumptions:

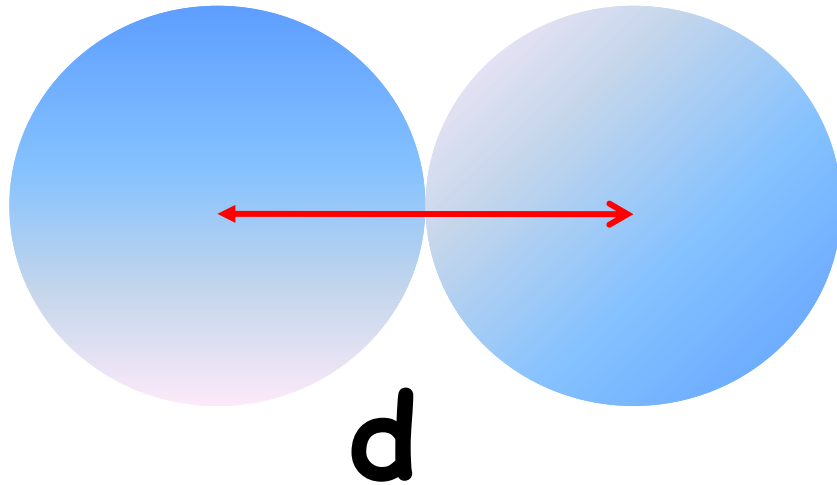
- + Our molecule is traveling with a constant speed  $v$  and all the other molecules are at rest.
- + All molecules are spheres of diameter  $d \rightarrow$  a collision occurs as the centers of 2 molecules come within a distance  $d$ .

To count the number of collisions:

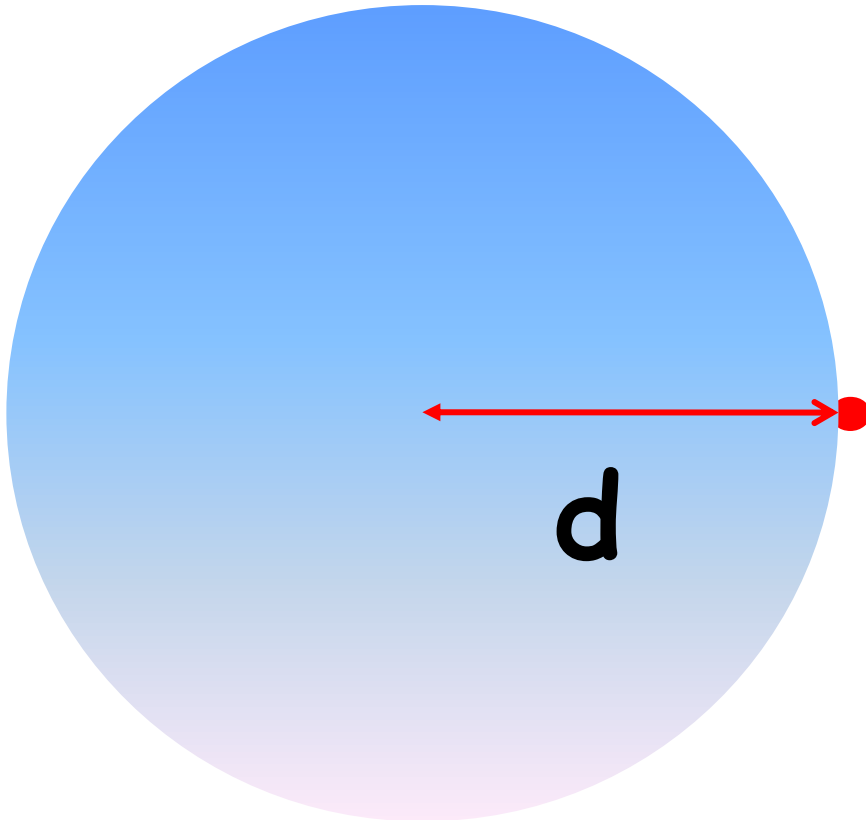
- + We further consider that this single molecule has an equivalent radius of  $d$  and all the other molecules are points (see cartoons next slides for an equivalent problem).



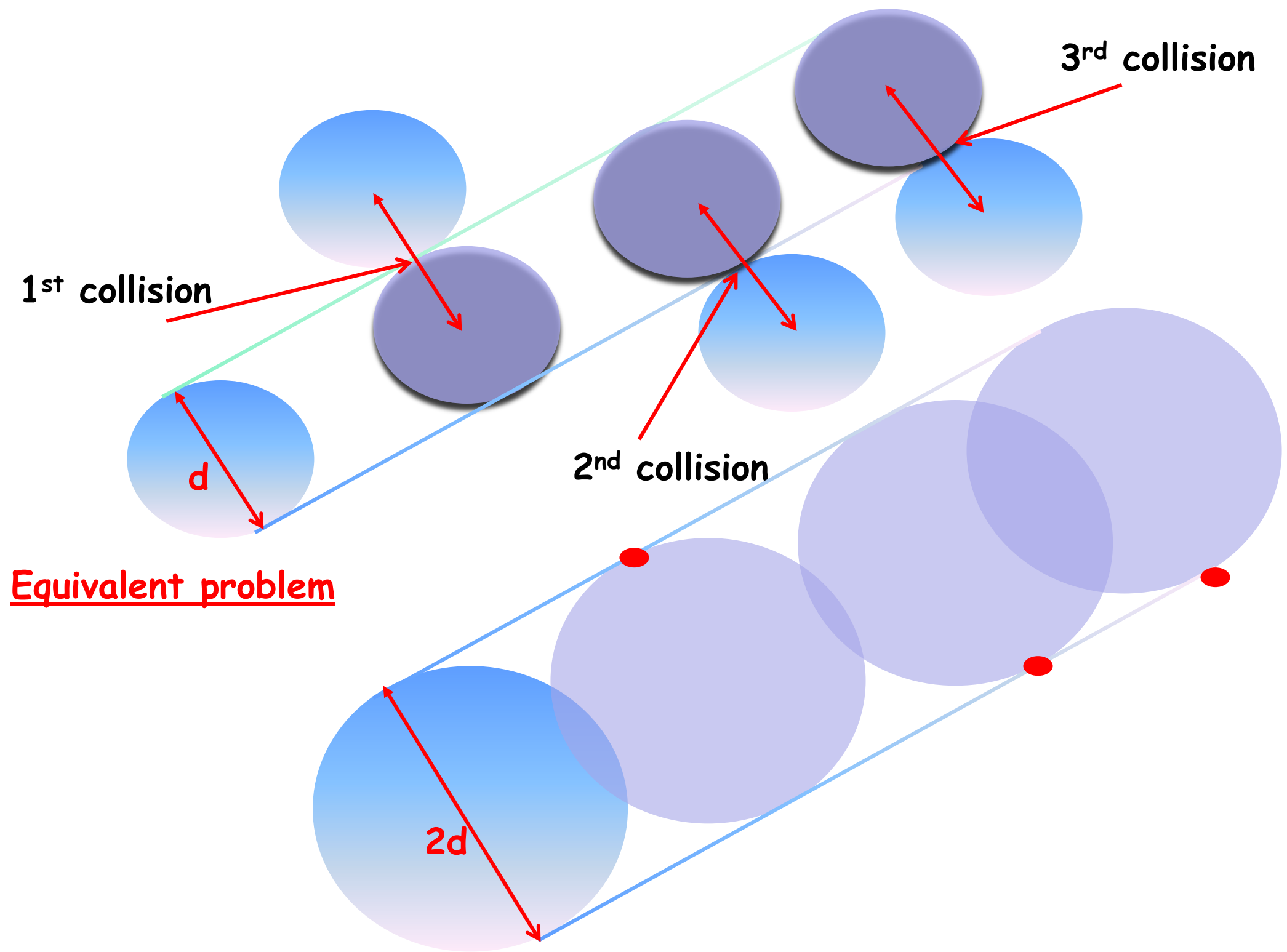
# Equivalent problem



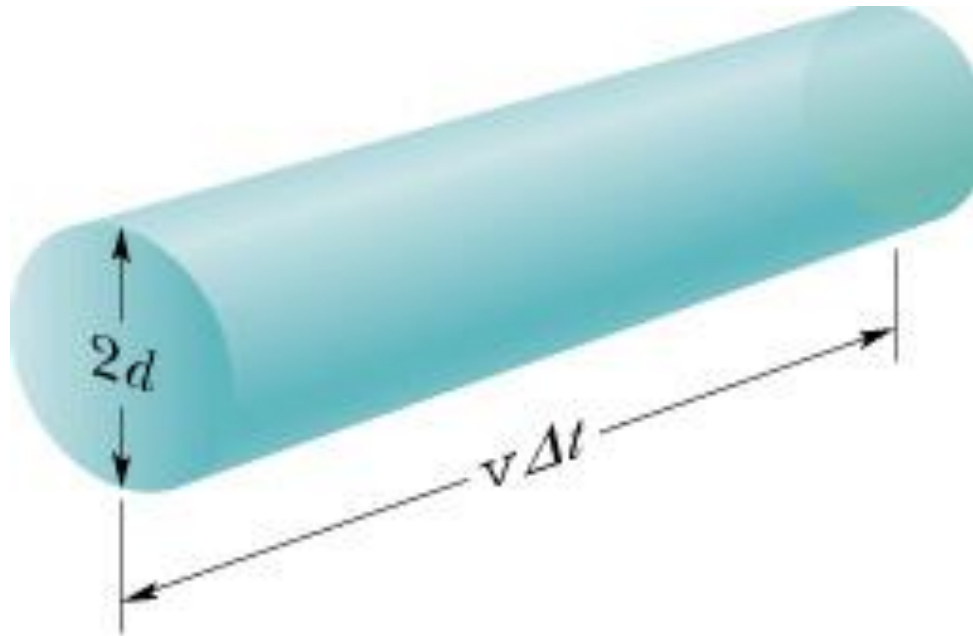
**= 1 collision**



**= 1 collision**



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



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

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

If all the molecules are moving:

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

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:

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

### 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  $\varepsilon$  then the frequency with which that state or condition occurs, or the probability of its occurrence is proportional to:

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

$k$  : the Boltzmann constant

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

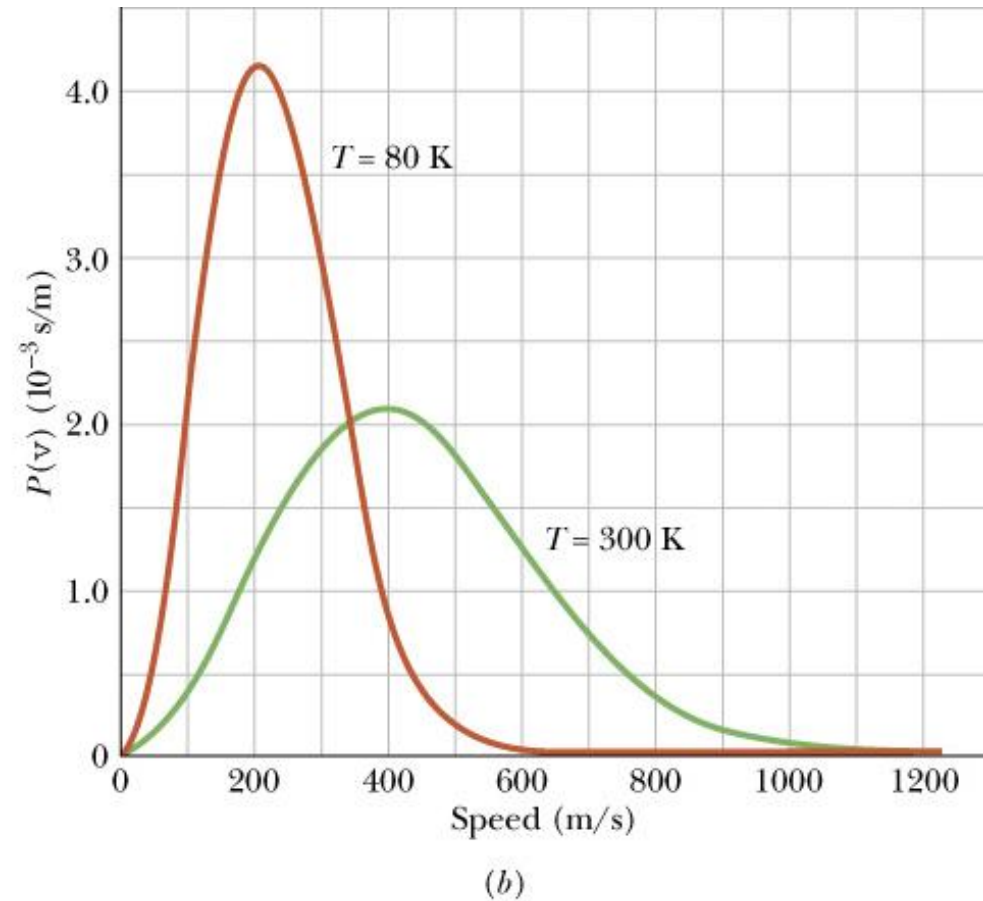
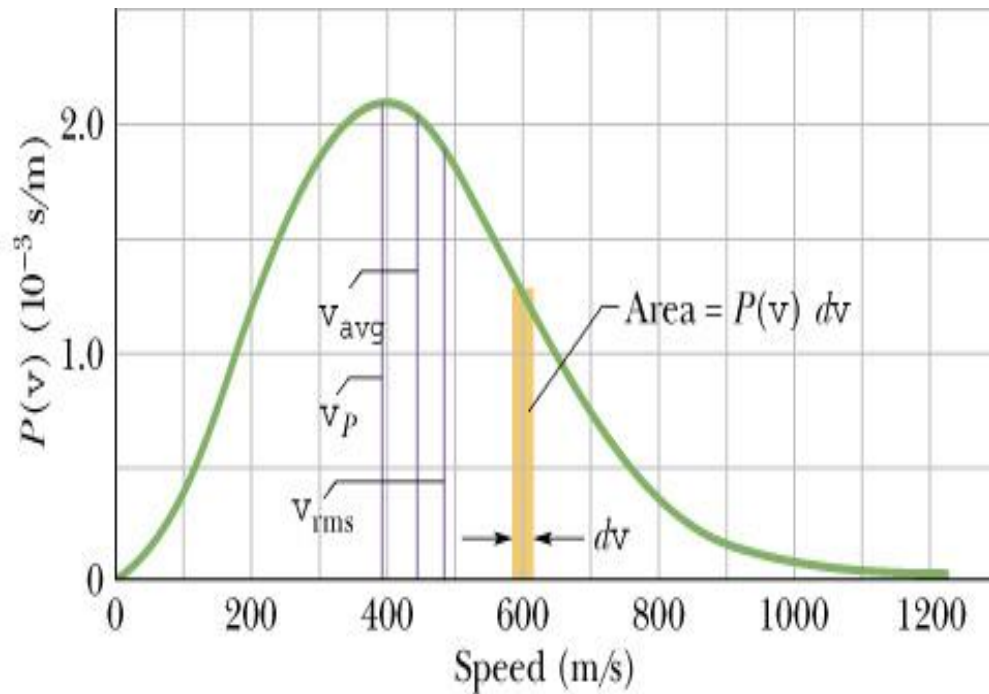
#### 3.3.1. The distribution of molecular speeds (or the Maxwell speed distribution law):

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

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



$P(v)dv$  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  $v_2$ :

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

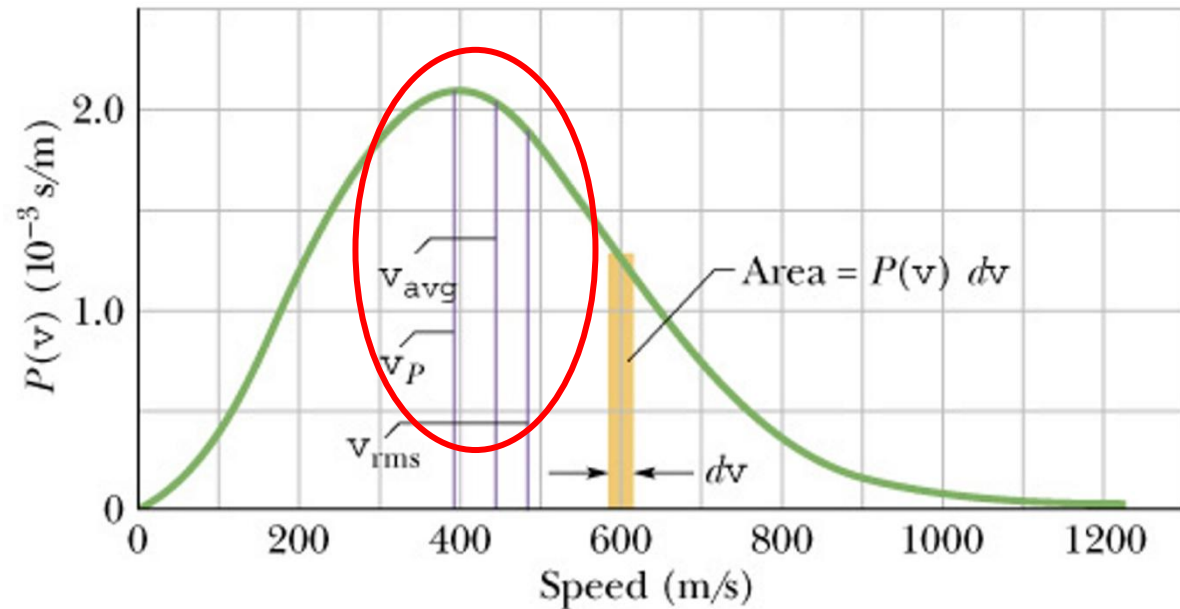
# Average, RMS, and Most Probable Speeds

The average speed:  $\bar{v} = \int_0^\infty vP(v)dv$  (2)

from (1) & (2):  $\bar{v} = \sqrt{\frac{8RT}{\pi M}}$

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

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



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:

$$\frac{dP(v)}{dv} = 0$$

$$v_P = \sqrt{\frac{2RT}{M}}$$

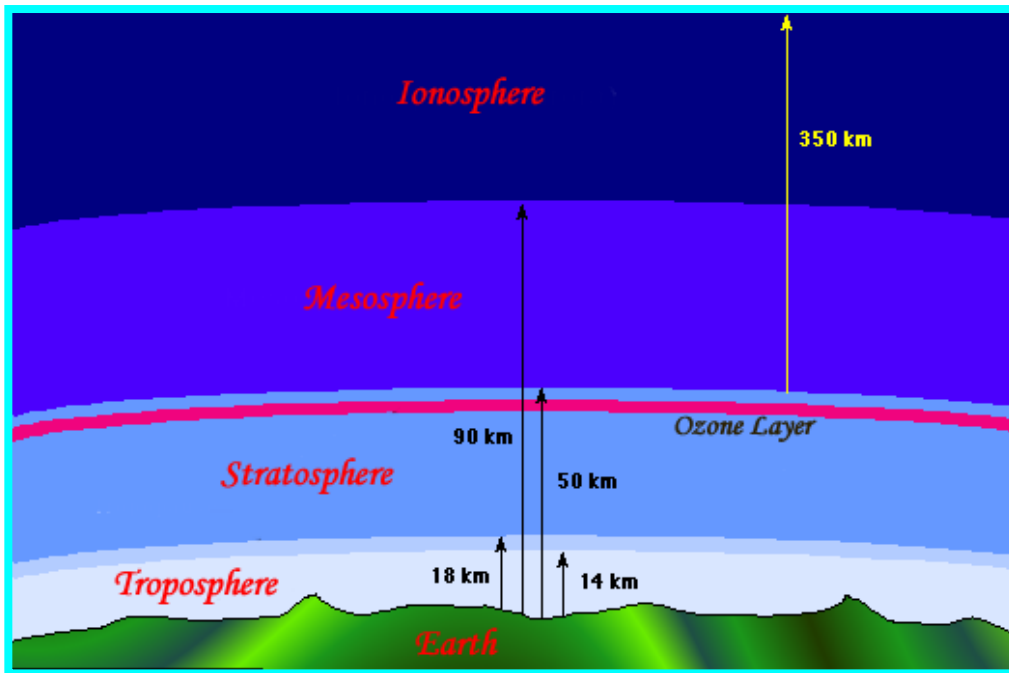
### 3.3.2. The barometric distribution law:

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.

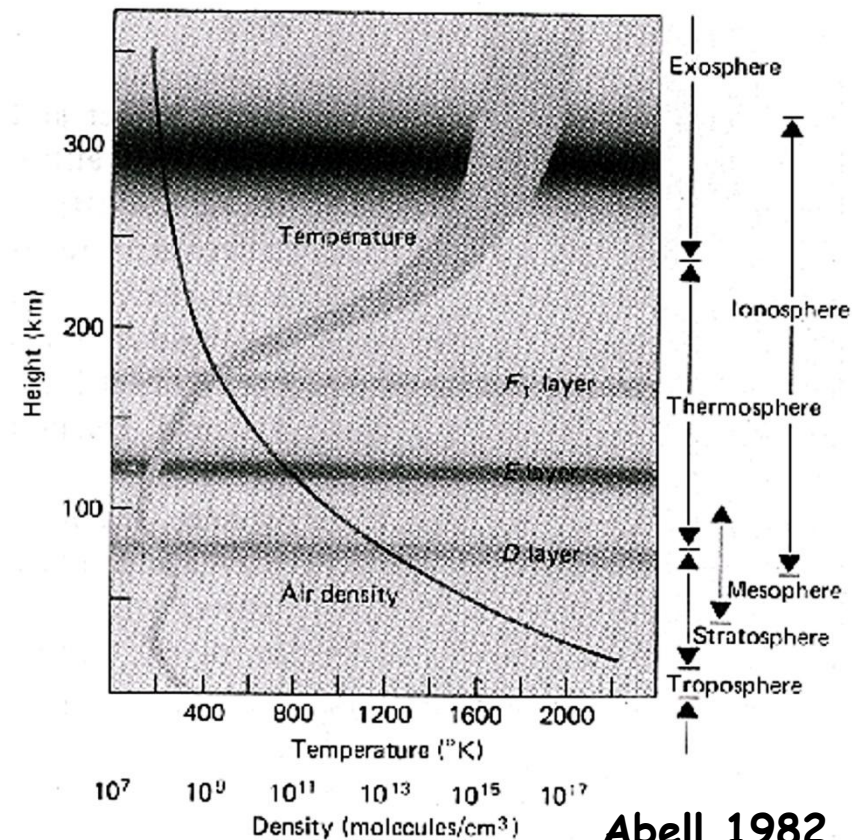
$$\rho(h) = \rho(h_0) e^{-mg(h-h_0)/kT}$$

where  $h_0$  is an arbitrary fixed reference height;  $m$  is the mass of a molecule.

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Homework: 25, 28, 32, 33, 40 (pages 532)

Not in Final