# Chapter 19 The Kinetic Theory of Gases

- 3 variables associated with a gas:
  - (1) **volume**: a result of the freedom the atoms have to spread throughout the container
  - (2) **pressure**: a result of the collisions of the atoms with the container's walls
  - (3) **temperature**: related to the kinetic energy of the atoms

### **Avogadro's Number**

One mole is the number of atoms in a 12g sample of carbon-12.

• Avogadro's number  $N_A = 6.02 \times 10^{23}$ /mole Avogadro's number

• Avogadro suggested that all gases occupying the same volume under the same conditions of temperature and pressure contain the same number of atoms or molecules.

• The number of moles  $n = \frac{N}{N}$ 

• the number of moles n in a sample from the mass  $M_{sam}$  of the sample and either the *molar mass* M (the mass of 1 mole) or the molecular mass m (the mass of one molecule):

$$n = \frac{M_{\text{sam}}}{M} = \frac{M_{\text{sam}}}{m N_A} \quad \Leftarrow \quad M = m N_A$$

#### **Ideal Gases**

• At low enough densities, all real gases tend to obey the relation

p V = n R T ideal gas law

*R* is the **gas constant**  $R = 8.31 \text{ J/mol} \cdot \text{K}$ .

• We can rewrite the equation in terms of the **Boltzmann constant**,



• On a *p*-*V* diagram, an *isotherm* is a curve that connects points that have the same temperature, ie, a graph of pressure versus volume for a gas whose temperature *T* is held constant.  $\begin{bmatrix} 1 \\ 0 \end{bmatrix} \begin{bmatrix} 1$ 

$$p = n R T \frac{1}{V} = (a \text{ constant}) \frac{1}{V}$$

• the isotherms with different temperatures doesn't cross each other.

• the work done by an ideal gas during an isothermal process

$$W = \int_{V_i}^{V_f} p \, \mathrm{d} V = \int_{V_i}^{V_f} \frac{n R T}{V} \, \mathrm{d} V \quad \Leftarrow \quad p V = n R T$$

• For an isothermal process:  $T = \text{const} \Rightarrow W = n R T \int_{V_i}^{V_f} \frac{\mathrm{d} V}{V} = n R T \ln V \Big|_{V_i}^{V_f}$ 

$$\Rightarrow W = n R T \ln \frac{V_f}{V_i} \quad \text{ideal gass}$$

leal gass, isothermal process

• For  $V_f > V_i$  (expansion), the work W done by an ideal gas is positive; For  $V_f < V_i$  (compression), the work W done by an ideal gas is negative.

#### **Work Done at Constant Volume and at Constant Pressure**

• If the volume of the gas is constant, then W = 0 constant-volume process



 $W = p (V_f - V_i) = p \Delta V$  constant-pressure process

problem 19-1

### **Pressure, Temperature, and RMS Speed**

• n moles of an ideal gas are confined in a cubical<sup>1.0</sup> box of volume V. The walls of the box are held at temperature T. We need to relate the macroscopic quantity - pressure p, to the microscopic quantity — the velocity of the molecule v.

• The molecules of gas in the box are moving in all directions and with various speeds, bouncing from the walls of the box.

 Ignore collisions of the molecules with one another and consider only elastic collisions with the walls.

• the change in the particle's momentum along the x axis is  $\Delta p_x = (-m v_x) - m v_x = -2 m v_x$ 





• the momentum  $\Delta p_x$  delivered to the wall by the molecule is  $+2mv_x$ .

• The molecule of will hit the wall repeatedly. The time  $\Delta t$  between collisions is the time the molecule takes to travel to the opposite wall and back again (a distance 2L) at speed  $v_x$   $\Lambda t = \frac{2L}{L}$ 

• the average rate at which momentum is delivered to the wall by this single molecule is  $\Delta p_x = 2 m v_x = m v_x^2$ 

$$\frac{\Delta p_x}{\Delta t} = \frac{2 m v_x}{2 L/v_x} = \frac{m v_x^2}{L}$$

 $\mathcal{V}_{r}$ 

• From Newton's 2<sup>nd</sup> law, the rate at which momentum is delivered to the wall is the force acting on that wall.

• Dividing the magnitude of the total force  $F_x$  by the area of the wall (= $L^2$ ) gives the pressure p on that wall.

• we can write this pressure:  $p = \frac{F_x}{L^2} = \frac{m v_{x1}^2 / L + \dots + m v_{xN}^2 / L}{L^2} = \frac{m}{L^3} \sum_{i=1}^N v_{xi}^2$   $(v_x^2)_{avg} = \frac{1}{N} \sum_{i=1}^N v_{xi}^2$ ,  $N = n N_A$  and  $M = N_A m$  the molar mass  $\Rightarrow \quad p = \frac{m}{L^3} \sum_{i=1}^N v_{xi}^2 = \frac{m}{V} N(v_x^2)_{avg} = \frac{n m N_A}{V} (v_x^2)_{avg} = \frac{n M (v_x^2)_{avg}}{V}$  • For any molecule,  $v^2 = v_x^2 + v_y^2 + v_z^2$ . Because there are many molecules and because they are all moving in random directions, the average values of the squares of their velocity components are equal, so that  $v_x^2 = v^2/3$ ,

$$p = \frac{n M (v^2)_{avg}}{3 V}$$
  
• root-mean-square speed  $v_{rms} \equiv \sqrt{(v^2)_{avg}} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} v_i^2} \Rightarrow p = \frac{n M v_{rms}^2}{3 V}$ 

• The equation tells how the pressure of the gas (a purely macroscopic quantity) depends on the speed of the molecules (a purely microscopic quantity).

• Using the ideal gas law (p V = n R T) gives

$$v_{\rm rms} = \sqrt{\frac{3 R T}{M}}$$

• The rms speed is only a kind of average speed; many molecules move much faster than this, and some much slower.

 The speed of sound in a gas is closely related to the rms speed of the molecules of that gas.

• If molecules move so fast, why does it take as long as a minute or so before you can smell perfume when someone opens a bottle across a room?

problem 19-3

#### **Translational Kinetic Energy**

 consider a single molecule of an ideal gas, Its average translational kinetic energy over the time is

$$K_{\text{avg}} = \left(\frac{1}{2} m v^2\right)_{\text{avg}} = \frac{1}{2} m (v^2)_{\text{avg}} = \frac{1}{2} m v_{\text{rms}}^2 = \frac{1}{2} m \frac{3 R T}{M} = \frac{3 R T}{2 N_A}$$
$$k = \frac{R}{N_A} \implies K_{\text{avg}} = \frac{3}{2} k T$$

At a given temperature T, all ideal gas molecules — no matter what their mass — have the same *average* translational kinetic energy — namely, 3kT/2. When we measure the temperature of a gas, we are also measuring the average translational kinetic energy of its molecules.

#### **Mean Free Path**

• the **mean free path**  $\lambda$ : is one useful parameter to describe this random motion of the molecules; it is the average distance traversed by a molecule between collisions.

• We expect (1)  $\lambda \propto V/N$  (2)  $\lambda \propto 1/d^2$ , the cross section of a molecule determines its effective target area, thus

$$\lambda = \frac{V}{\sqrt{2} \pi N d^2} \quad \text{mean free path}$$

#### justification

• A collision will then take place if the centers of 2 molecules come within a distance *d* of each other.

• As a single molecule zigzags through the gas, it sweeps out a cylinder of cross-sectional area  $\pi d^2$  between successive collisions.

• For a time interval  $\Delta t$ , it moves a distance  $v_{avg}\Delta t$ .

• The volume of the cylinder is  $(\pi d^2)(v_{avg}\Delta t)$ .

• The number of collisions that occur in time  $\Delta t$  is equal to the number of molecules that lie within this cylinder,

 $\lambda = \frac{\text{length of path during } \Delta t}{\text{number of collisions in } \Delta t} = \frac{v_{\text{avg}} \Delta t}{\pi d^2 v_{\text{rel}} \Delta t N/V} = \frac{v_{\text{avg}}}{\pi d^2 v_{\text{rel}} N/V}$ 

 $v_{avg}$ : the mean speed of the molecules *relative to the container*;

 $v_{\rm rel}$ : the mean speed of a single molecule *relative to the other molecules*.



• A detailed calculation, taking into account the actual speed distribution of the molecules, gives V

$$v_{\rm rel} = \sqrt{2} v_{\rm avg} \quad \Rightarrow \quad \lambda = \frac{V}{\sqrt{2} \pi N d^2}$$

The mean free path of air molecules: 0.1µm for H=0; 16cm for H=100km; 20km for H=300km.

problem 19-4

### **The Distribution of Molecular Speeds**



### Random molecular velocities



 $v_{\rm rel}^2 = \vec{v}_{\rm rel}^2 = (\vec{v}_1 - \vec{v}_2) \cdot (\vec{v}_1 - \vec{v}_2) = \vec{v}_1 \cdot \vec{v}_1 - 2 \vec{v}_1 \cdot \vec{v}_2 + \vec{v}_2 \cdot \vec{v}_2$ 

$$\Rightarrow \quad \overline{v}_{\rm rel} = \overline{\sqrt{\vec{v}_1 \cdot \vec{v}_1 - 2 \vec{v}_1 \cdot \vec{v}_2 + \vec{v}_2 \cdot \vec{v}_2}}$$

$$= \sqrt{\vec{v}_{1} \cdot \vec{v}_{1}} - 2 \, \vec{v}_{1} \cdot \vec{v}_{2} + \vec{v}_{2} \cdot \vec{v}_{2}}$$

$$= \sqrt{\overline{v}_1^2 + \overline{v}_2^2}$$

 $\vec{v}_1$ 

$$=\sqrt{\overline{v}^2+\overline{v}^2}$$

$$=\sqrt{2} \overline{v}$$

• The quantity P(v) is a probability distribution function: For any speed v, the product P(v)dv (a dimensionless quantity) is the fraction of molecules with speeds in the interval dv centered on speed v,  $\int_{0}^{\infty} P(v) dv = 1$ 

• The fraction (frac) of molecules with speeds in an interval of  $v_1$  to  $v_2$  is

$$\operatorname{frac} = \int_{v_1}^{v_2} P(v) \, \mathrm{d} v$$

#### **Average, RMS, and Most Probable Speeds**

• find the **average speed**  $v_{avg}$  of the molecules in a gas with the distribution law

$$v_{\rm avg} = \int_0^\infty v P(v) \, \mathrm{d} v$$

• Substituting for P(v) from the Maxwell's speed distribution law and find

$$v_{\rm avg} = \sqrt{\frac{8 R T}{\pi M}}$$
 average speed

• Similarly,  $(v^2)_{avg} = \int_0^\infty v^2 P(v) dv = \frac{3 R T}{M} \Rightarrow \left| v_{rms} = \sqrt{(v^2)_{avg}} = \sqrt{\frac{3 R T}{M}} \right|$  rms speed

• The most probable speed  $v_P$  is the speed at which P(v) is maximum, therefore solve it to find

$$\frac{\mathrm{d} P}{\mathrm{d} v} = 0 \quad \Rightarrow \quad v_P = \sqrt{\frac{2 R T}{M}} \quad \text{most probable speed}$$

Gaussian Integral 
$$\int_{-\infty}^{\infty} e^{-x^2} dx = 2 \int_{0}^{\infty} e^{-x^2} dx = \sqrt{\pi}$$

Proof:

$$\left(\int_{-\infty}^{\infty} e^{-x^2} dx\right)^2 = \int_{-\infty}^{\infty} e^{-x^2} dx \int_{-\infty}^{\infty} e^{-y^2} dy = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(x^2+y^2)} dx dy$$

$$= \int_0^\infty \int_0^{2\pi} e^{-r^2} (r \,\mathrm{d}\,\theta) (\mathrm{d}\,r) \quad \Leftarrow \quad \begin{array}{l} r^2 = x^2 + y^2 \\ \mathrm{d}\,x \,\mathrm{d}\,y = (r \,\mathrm{d}\,\theta) (\mathrm{d}\,r) = r \,\mathrm{d}\,r \,\mathrm{d}\,\theta \end{array}$$

$$= \int_0^{2\pi} \mathrm{d}\,\theta \int_0^\infty e^{-r^2} r \,\mathrm{d}\,r = 2\pi \cdot \frac{1}{2} \int_0^\infty e^{-q} \,\mathrm{d}\,q \quad \Leftarrow \quad q \equiv r^2$$

$$=-\pi e^{-q}\Big|_0^\infty = \pi$$

$$s \equiv \sqrt{\frac{2 M^3}{\pi R^3 T^3}}, \quad u^2 = \frac{2 R T}{M} \quad \Rightarrow \quad P(v) = s v^2 e^{-v^2/u^2}$$

$$\int_{0}^{\infty} P(v) dv = s \int_{0}^{\infty} v^{2} e^{-v^{2}/u^{2}} dv = \frac{s}{2} \int_{0}^{\infty} v e^{-v^{2}/u^{2}} dv^{2} = -\frac{s u^{3}}{2} \int_{0}^{\infty} \frac{v}{u} de^{-v^{2}/u^{2}}$$
$$= -\frac{s u^{3}}{2} \left[ \frac{v}{u} e^{-v^{2}/u^{2}} \Big|_{0}^{\infty} - \int_{0}^{\infty} e^{-v^{2}/u^{2}} d\frac{v}{u} \right] = \frac{s u^{3}}{2} \int_{0}^{\infty} e^{-v^{2}/u^{2}} d\frac{v}{u} = \frac{s u^{3}}{2} \frac{\sqrt{\pi}}{2} = 1$$

$$\overline{v} = \int_0^\infty v P(v) dv = s \int_0^\infty v^3 e^{-v^2/u^2} dv = \frac{s u^4}{2} \int_0^\infty q e^{-q} dq \quad \Leftrightarrow \quad q \equiv \frac{v^2}{u^2}$$
$$= -\frac{s u^4}{2} [q e^{-q} \Big|_0^\infty - \int_0^\infty e^{-q} dq] = -\frac{s u^4}{2} e^{-q} \Big|_0^\infty = \sqrt{\frac{8 R T}{\pi M}}$$

$$\overline{v^2} = \int_0^\infty v^2 P(v) \, \mathrm{d} \, v = s \int_0^\infty v^4 \, e^{-v^2/u^2} \, \mathrm{d} \, v = \frac{s \, u^5}{2} \int_0^\infty x^3 \, e^{-x^2} \, \mathrm{d} \, x^2 \quad \Leftarrow \quad x \equiv \frac{v}{u}$$
$$= -\frac{s \, u^5}{2} \left[ x^3 \, e^{-x^2} \Big|_0^\infty - \frac{3}{2} \int_0^\infty x \, e^{-x^2} \, \mathrm{d} \, x^2 \right] = -\frac{3 \, s \, u^5}{4} \int_0^\infty x \, \mathrm{d} \, e^{-x^2} = \frac{3 \, s \, u^5}{4} \frac{2}{s \, u^3} = \frac{3 \, R \, T}{M}$$

• some molecules will have speeds that are many times of  $v_P$ . These molecules form the *high-speed tail* of a distribution curve, useful for rain & sunshine.

problem 19-5, 19-6

### The Molar Specific Heats of an Ideal Gas

### Internal Energy $E_{int}$

• assume that our ideal gas is a *monatomic gas* and the internal energy  $E_{int}$  of the ideal gas is simply the sum of the translational kinetic energies of its atoms.

• The average translational kinetic energy of a single atom depends only on the gas temperature, ie,  $K_{avg} = 3kT/2$ . The internal energy of a sample of *n* moles of the gas is  $E_{avg} = -(nN_{avg}) \left(\frac{3}{2}k_{avg} - (nN_{avg}) \left(\frac{3}{2}k_{avg} - (nN_{avg})\right) \left(\frac{3}{2}k_{avg} - (n$ 

$$E_{\rm int} = (n N_A) K_{\rm avg} = (n N_A) (\frac{3}{2} k T) = (n N_A) (\frac{3 K}{2 N_A} T)$$

 $\Rightarrow \quad E_{\text{int}} = \frac{3}{2} n R T \quad \text{monatomic ideal gas}$ 

The internal energy  $E_{int}$  of an ideal gas is a function of the gas temperature only; it does not depend on any other variable.

- 2 types of the molar specific heat of an ideal gas:
  - $C_V$ : molar specific heat at constant volume;
  - $C_p$ : molar specific heat at constant pressure.



Volume

A change in the internal energy  $E_{\rm int}$  of a confined ideal gas depends on the change in the gas temperature only; it does not depend on what type of process produces the change in the temperature.

• Although the values of heat Q and work W associated with these 3 paths differ, the values of  $\Delta E_{int}$  associated with them are identical because they all involve the same temperature change  $\Delta T$ .

### **Molar Specific Heat at Constant Pressure**

• Q is related to the temperature change  $\Delta T$  by

 $Q = n C_p \Delta T$ constant pressure • This  $C_p$  is greater than the molar specific heat at constant volume  $C_V$ , because energy must because energy must now be supplied not only to raise the temperature of the gas but also for the gas to do work.





Volume

• From the 1<sup>st</sup> law of thermodynamics

$$n C_{V} \Delta T \Leftarrow \Delta E_{int} = Q - W = n C_{p} \Delta T - p \Delta V = n C_{p} \Delta T - n R \Delta T$$
  

$$\Rightarrow C_{V} = C_{p} - R \Rightarrow C_{p} = C_{V} + R$$
(a) He

problem 19-7

### **Degrees of Freedom and Molar Specific Heats**

 $\bullet$  to explain the discrepancy by considering the possibility that molecules with more than one atom can store internal  $^{\rm O}$  energy in forms other than translational kinetic energy.

 assume that all 3 types (monatomic, diatomic, polyatomic) of molecules can have translational motions, and rotational motions.

 assume that the diatomic and polyatomic molecules can have oscillatory motions.

• the theorem of the **equipartition of energy**:

Every kind of molecule has a certain number f, *degrees* of freedom, which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with it - on average - an energy of kT/2 per molecule (or RT/2 per mole).

H H (c) CH<sub>4</sub>

 $(b) \mathbf{O}_{\mathbf{9}}$ 

Η

• For the translational motion, the molecules have velocity components along xyz axes. Thus, gas molecules of all types have 3 degrees of translational freedom and, on average, an associated energy of 3( kT/2 ) per molecule.

• A monatomic gas molecule does not rotate and so has no rotational energy.

• A diatomic molecule can rotate only about axes perpendicular to the line connecting the atoms and have only 2 degrees of rotational freedom and a rotational energy of only 2(kT/2) per molecule.

• Only the polyatomic molecules are able to rotate with an angular velocity component along each of the 3 axes, and have 3 degrees of rotational freedom, and an energy of 3(kT/2) per molecule.

• Now the internal energy: 
$$E_{\text{int}} = \frac{f}{2} n R T \Rightarrow C_V = \frac{f}{2} R = 4.16 f \text{ J/mol} \cdot \text{K}$$

where f is the number of degrees of freedom.

• f = 3 for monatomic gases, f = 5 for diatomic gases, f = 6 for polyatomic gases. **Degrees of Freedom for Various Molecules** 

		Degree of Freedon		n specific heat		
Molecule	Example	Translational	Rotational	Total $(f)$	$C_{V}$	$C_p$
monatomic	He	3	0	3	$\frac{3}{2}R$	$\frac{5}{2}R$
diatomic	$O_2$	3	2	5	$\frac{5}{2}R$	$\frac{7}{2}R$
polyatomic	CH <sub>4</sub>	3	3	6	3 <i>R</i>	4 <i>R</i>

### **A Hint of Quantum Theory**

• improve the agreement of kinetic <sup>4</sup> theory by including the oscillations of the atoms in a gas of diatomic or polyatomic molecules. <sup>3</sup>

 experiment shows that such oscillations are "turned on" only when the gas molecules have relatively large energies.

 quantum theory shows that rotational motion of the molecules requires a certain minimum amount
 20
 50
 100
 200
 500
 100
 Temperature (K)
 Temperature (K)

## The Adiabatic Expansion of an Ideal Gas

• ensure that Q = 0 either by carrying out the process very quickly (as in sound waves) or by doing it (at any rate) in a well-insulated container.

• the relation between the pressure and the volume during an adiabatic process is  $p V^{\gamma} = a \text{ constant}$  adiabatic process

in which  $\gamma = C_p/C_V$ , the ratio of the molar specific heats for the gas.





#### Proof

• the 1<sup>st</sup> law of thermodynamics:

 $n C_V d T \leftarrow d E_{int} = Q - p d V = -p d V \implies n d T = -\frac{p}{C_V} d V$  (a)

• Now from the ideal gas law (p V = n R T) we have

$$n R d T = p d V + V d p \implies n d T = \frac{p d V + V d p}{C_p - C_V}$$
 (b)  $\Leftarrow R = C_p - C_V$ 

• Combining (a) & (b) gives

$$\frac{\mathrm{d} p}{p} + \frac{C_p}{C_V} \frac{\mathrm{d} V}{V} = 0 \quad \Rightarrow \quad \ln p + \gamma \ln V = \mathrm{a \ const} \quad \Rightarrow \quad p \ V^{\gamma} = \mathrm{a \ constant}$$

$$\begin{bmatrix} -\frac{p}{C_V} dV = \frac{p dV + V dp}{C_p - C_V} \end{bmatrix} \times (C_p - C_V)$$
  

$$\Rightarrow \quad -\frac{C_p - C_V}{C_V} p dV = p dV + V dp$$
  

$$\Rightarrow \quad (1 - \gamma) p dV = p dV + V dp$$

$$\Rightarrow \quad \gamma \ p \ d \ V + V \ d \ p = 0$$
$$\Rightarrow \quad \int_{i}^{f} \left[ \frac{d \ p}{p} + \gamma \frac{d \ V}{V} = 0 \right]$$

 $\Rightarrow \quad \ln p + \gamma \ln V = \text{const}$ 

• Since the gas goes from an initial state i to a final state f,

 $p_i V_i^{\gamma} = p_f V_f^{\gamma}$  adiabatic process

• use the ideal gas equation (p V = n R T) to eliminate p,

 $\frac{n R T}{V} V^{\gamma} = \text{a constant} \quad \Rightarrow \quad T V^{\gamma-1} = \text{a constant} \quad \text{adiabatic process}$ 

• When the gas goes from an initial state i to a final state f, we can rewrite

 $T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$  adiabatic process

• Understanding adiabatic processes allows you to understand why popping the cork on a cold bottle of champagne or the tab on a cold can of soda causes a slight fog to form at the opening of the container.

#### **Free Expansions**

• Since a free expansion is not in equilibrium, the equation of the adiabatic expansion can not apply to it.

• In a free expansion, because  $\Delta E_{int} = 0$ , the temperature of the final int state must be that of the initial state, ie,  $T_i = T_f$ , and  $p_i V_i = p_f V_f$ .





Selected problems: 6, 14, 23, 41