

# Contents

<b>19 The kinetic theory of gases</b>	<b>1</b>
19.1 Avogadro's Number . . . . .	1
19.2 Ideal Gases . . . . .	2
19.2.1 Work done by an ideal gas at constant temperature . .	3
19.2.2 Work done by an ideal gas at constant volume . . . . .	3
19.2.3 Work done by an ideal gas at constant pressure . . . . .	4
19.3 Ideal Gas Pressure, Temperature and RMS Speed . . . . .	4
19.3.1 Translational kinetic energy . . . . .	5
19.4 Mean Free Path . . . . .	6
19.5 The Distribution of Molecular Speeds . . . . .	8
19.5.1 Average, RMS, and most probable speeds . . . . .	10
19.5.2 Optional: average relative speed . . . . .	12
19.6 The Molar Specific Heats of an Ideal Gas . . . . .	12
19.6.1 Internal energy of an ideal gas . . . . .	12
19.6.2 Molar specific heat $C_V$ at constant volume . . . . .	13
19.6.3 Molar specific heat $C_p$ at constant pressure . . . . .	14
19.7 Degrees of Freedom and Molar Specific Heats . . . . .	15
19.7.1 A Hint of Quantum Theory . . . . .	15
19.8 Adiabatic Expansion of an Ideal Gas . . . . .	17
19.8.1 Free expansion . . . . .	18

## 19 The kinetic theory of gases

In this chapter we will introduce the kinetic theory of gases which relates the motion of the constituent atoms to the volume, pressure and temperature of the gas. The following topics will be covered:

Ideal gas law. Internal energy of an ideal gas. Distribution of speeds among the atoms in a gas. Specific heat under constant volume. Specific heat under constant volume. Adiabatic expansion of an ideal gas.

### 19.1 Avogadro's Number

A mole of any substance is defined as the quantity contained in a mass equal to the molar mass of the substance. The mole of any substance contains the

same number of atoms (or molecules). This is known as:

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

The number  $n$  of moles in a mass  $M_{\text{sample}}$  of a substance is given by the ratio:

$$n = \frac{M_{\text{sample}}}{M}$$

Here  $M$  is the molar mass of the substance. The number

$$n = \frac{N}{N_A}$$

Here  $N$  is the number of atoms in the mass  $M_{\text{sample}}$ . The mass

$$M_{\text{sample}} = Nm.$$

Here  $m$  is the mass of each molecule.

## 19.2 Ideal Gases

It was found experimentally that 1 mole of any gas if placed in a containers that have the same volume  $V$  and kept at the same temperature  $T$ , approximately all have the same pressure  $p$ . The small differences in pressure disappear if lower gas densities are used. Further experiments showed that all low density gases obey the equation:

$$pV = nRT \text{ (ideal gas law)}$$

Here

$$R = 8.31 \text{ J/mol} \cdot \text{K}$$

and is known as the gas constant. The equation itself is known as the ideal gas law. The constant  $R$  can be expressed as:

$$R = kN_A$$

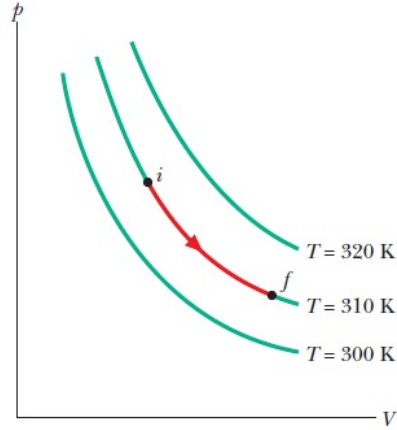
Here  $k$  is called the Boltzmann constant and it is equal to  $1.38 \times 10^{-23} \text{ J/K}$ . If we substitute  $R$  as well as  $n = \frac{N}{N_A}$  in the ideal gas law we get the equivalent form:

$$pV = NkT \text{ (ideal gas law)}$$

Here  $N$  is the number of molecules in the gas. The behavior of all real gases approaches that of an ideal gas at low enough densities. Low densities means that the gas molecules are far enough apart that they do not interact with one another, but only with the walls of the gas container.

### 19.2.1 Work done by an ideal gas at constant temperature

Consider the gas shown in the figure.



It is held at a constant temperature  $T$  and under goes an isothermal expansion from volume  $V_i$  to volume  $V_f$ . The process follows the red line on the lower figure. The work  $W$  done by the ideal gas is given by the equation:

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

From the ideal gas law we have that

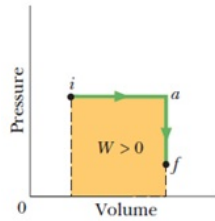
$$p = \frac{nRT}{V} \rightarrow W = \int_{V_i}^{V_f} \frac{nRT}{V} dV = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT [\ln V]_{V_i}^{V_f}$$

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

For expansion we have :  $V_f > V_i \rightarrow \ln \frac{V_f}{V_i} > 0 \rightarrow W > 0$

For compression we have :  $V_f < V_i \rightarrow \ln \frac{V_f}{V_i} < 0 \rightarrow W < 0$

### 19.2.2 Work done by an ideal gas at constant volume



Consider process  $a \rightarrow f$ . During this process the volume of the ideal gas is kept constant. Thus the work  $W$  done by the gas is:

$$W = \int p dV = 0$$

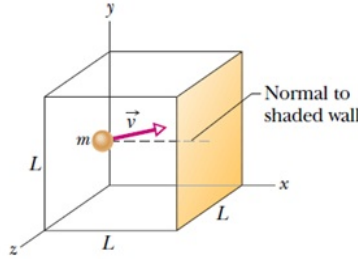
### 19.2.3 Work done by an ideal gas at constant pressure

Consider process  $i \rightarrow a$ . During this process the pressure is kept constant at  $p$  and the volume changes from  $V_i$  to  $V_f$ . The work  $W$  done by the gas is:

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

## 19.3 Ideal Gas Pressure, Temperature and RMS Speed

Consider the molecule of mass  $m$  moving inside a container of dimensions  $L \times L \times L$  as shown in the figure.



We will follow the motion of the molecule along the x-axis. The molecule will hit the shaded wall repeatedly. The time  $\Delta t$  between the collisions is the time the molecule takes to travel to the opposite wall and back again (a distance of  $2L$ ) at speed  $v_x$ . Thus

$$\Delta t = \frac{2L}{v_x}$$

The ratio

$$\frac{\Delta p_x}{\Delta t} = \frac{mv_x - (-mv_x)}{\Delta t} = \frac{2mv_x}{\frac{2L}{v_x}} = \frac{mv_x^2}{L} = F_x$$

Here  $\Delta p_x$  is the momentum transfer to the wall. The force exerted by one molecule  $F_x = \frac{\Delta p_x}{\Delta t}$ . Thus the pressure  $p$  exerted by all the molecules on the wall is given by:

$$p = \frac{F_x}{L^2} = \frac{mv_{x1}^2/L + mv_{x2}^2/L + \dots + mv_{xN}^2/L}{L^2} = \frac{m}{L^3} (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2)$$

The root mean square (RMS) value for  $v_x$  is defined as:

$$\langle v_x^2 \rangle = \frac{v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2}{N} \rightarrow (v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2) = N \langle v_x^2 \rangle$$

Thus the gas pressure

$$p = \frac{Nm}{L^3} \langle v_x^2 \rangle$$

For each molecule the speed

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

The average values of the squares for each component are equal. Thus:

$$\langle v_x^2 \rangle = \frac{\langle v_x^2 + v_y^2 + v_z^2 \rangle}{3} = \frac{\langle v^2 \rangle}{3} = \frac{v_{rms}^2}{3}$$

This equation tells us how the gas pressure depends on the speed of the gas molecules. If we solve this equation for  $v_{rms}$ , we get:

$$v_{rms} = \sqrt{3 \langle v_x^2 \rangle} = \sqrt{\frac{3L^3 p}{Nm}} = \sqrt{\frac{3pV}{Nm}} = \sqrt{\frac{3pV}{nM}}$$

### 19.3.1 Translational kinetic energy

The kinetic energy of a gas molecule  $K = \frac{1}{2}mv^2$ . Its average kinetic energy

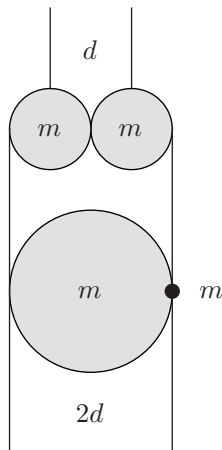
$$\langle K \rangle = \frac{1}{2}m \langle v^2 \rangle = \frac{3pV}{2N} = \frac{3}{2}kT$$

At a given temperature  $T$ , all ideal gas molecules, no matter what their mass, have the same average translational kinetic energy. When we measure the temperature of a gas, we are also measuring the average translational kinetic energy of its molecules.

## 19.4 Mean Free Path

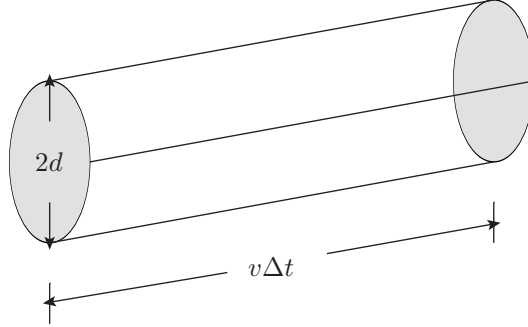
A molecule travelling through a gas will collide with other gas molecules in its path. Between collisions, the molecule moves in a straight line at constant speed. One useful parameter to describe the random motion is the mean free path  $\lambda$  of the molecules. As its name implies,  $\lambda$  is the average distance traversed by a molecule between collisions. We expect  $\lambda$  to vary inversely with  $\frac{N}{V}$ , the number of molecules per unit volume. We also expect  $\lambda$  to vary inversely with the size of the molecules. The larger the molecules are, the smaller the mean free path.

We assume that the molecules are spheres of diameter  $d$ . A collision will take place if the centers of two molecules come within a distance  $d$  of each other. Another, more helpful way to look at the situation is to consider our single molecule to have a radius of  $d$  and all the other molecules to be points.



This does not change our criterion for a collision.

As our single molecule zigzags through the gas, it sweeps out a short cylinder of cross-sectional area  $\pi d^2$  between successive collisions. If we watch this molecule for a time interval  $\Delta t$ , it moves a distance  $v\Delta t$ , where  $v$  is its assumed speed. Thus if we align all the short cylinders swept out in interval  $\Delta t$ , we form a complete cylinder of length  $v\Delta t$  and volume  $(\pi d^2)(v\Delta t)$ .



The number of collisions that occur in time  $\Delta t$  is then equal to the number of (point) molecules that line within this cylinder.

Since  $\frac{N}{V}$  is the number of molecules per unit volume, the number of molecules in the cylinder is

$$\frac{N}{V} (\pi d^2) (v \Delta t)$$

This is also the number of collisions in time  $\Delta t$ . The mean free path is the length of path divided by this number

$$\lambda = \frac{\text{length of path during } \Delta t}{\text{number of collisions in } \Delta t} = \frac{v \Delta t}{\frac{N}{V} (\pi d^2) (v \Delta t)} = \frac{1}{\pi d^2 \frac{N}{V}} \quad (1)$$

This equation is only approximate because it is based on the assumption that all the molecules except one are at rest. In fact, all the molecules are moving. When this is taken properly into account, a factor of  $\frac{1}{\sqrt{2}}$  needs to be inserted and the mean free path turns out to be

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

The reason that results in this  $\frac{1}{\sqrt{2}}$  factor is because the two  $v$  symbols involved in (1) are in fact different. The  $v$  in the numerator is  $v_{avg}$ , the mean speed of the molecules relative the the container. The  $v$  in the denominator is  $v_{rel}$ , the mean speed of our single molecule relative to the other molecules, which are moving. It is this latter average speed that determines the number of collisions. A detailed calculation, taking into account the actual speed distribution of the molecules, gives  $v_{rel} = \sqrt{2} v_{avg}$  and thus the  $\frac{1}{\sqrt{2}}$  factor.

## 19.5 The Distribution of Molecular Speeds

The root mean square speed  $v_{rms}$  gives a general idea of molecular speeds at a temperature  $T$ . More complete information is given by Maxwell's speed distribution law. This can be derived from the assumption that the probability of finding a molecule with energy  $E$  is proportional to  $e^{-\frac{E}{kT}}$ . For ideal gas, the energy of a molecule is

$$E = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2).$$

The probability of finding of a molecule with x-component of the velocity in the range of  $(v_x, v_x + dv_x)$ , y-component in the range of  $(v_y, v_y + dv_y)$ , and z-component in  $(v_z, v_z + dv_z)$  is equal to

$$\begin{aligned} P(v_x, v_y, v_z) dv_x dv_y dv_z &= C e^{-\frac{\frac{1}{2}mv^2}{kT}} dv_x dv_y dv_z \\ &= C e^{-\frac{\frac{1}{2}mv_x^2}{kT}} e^{-\frac{\frac{1}{2}mv_y^2}{kT}} e^{-\frac{\frac{1}{2}mv_z^2}{kT}} dv_x dv_y dv_z \end{aligned}$$

The proportionality constant  $C$  can be determined from the normalization condition that

$$\begin{aligned} 1 &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P(v_x, v_y, v_z) dv_x dv_y dv_z \\ &= C \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\frac{\frac{1}{2}mv^2}{kT}} dv_x dv_y dv_z \\ &= C \int_{-\infty}^{\infty} e^{-\frac{\frac{1}{2}mv_x^2}{kT}} dv_x \int_{-\infty}^{\infty} e^{-\frac{\frac{1}{2}mv_y^2}{kT}} dv_y \int_{-\infty}^{\infty} e^{-\frac{\frac{1}{2}mv_z^2}{kT}} dv_z \\ &= C \left( \int_{-\infty}^{\infty} e^{-\frac{\frac{1}{2}ms^2}{kT}} ds \right)^3 \end{aligned} \tag{3}$$

Let us evaluate the integral:

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

Let  $r^2 = x^2 + y^2$ . The area for the region between two concentric circles of radii  $r$  and  $r + dr$  is  $2\pi r dr$ . The above integral can be written as

$$\int_0^{\infty} e^{-\alpha r^2} 2\pi r dr = \pi \int_0^{\infty} e^{-\alpha r^2} d(r^2) = \frac{\pi}{\alpha}$$



Therefore, we have

$$\int_{-\infty}^{\infty} e^{-\alpha s^2} ds = \sqrt{\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-\alpha(x^2+y^2)} dx dy} = \sqrt{\frac{\pi}{\alpha}} \quad (4)$$

With  $\alpha = \frac{m}{2kT}$  and the normalization condition (3), we get

$$C = \frac{1}{\left(\sqrt{\frac{\pi}{\alpha}}\right)^3} = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} = \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} \quad (5)$$

The probability density  $P(v_x, v_y, v_z)$  then can be written as

$$P(v_x, v_y, v_z) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{\frac{1}{2}mv^2}{kT}} = \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} e^{-\frac{Mv^2}{2RT}}$$

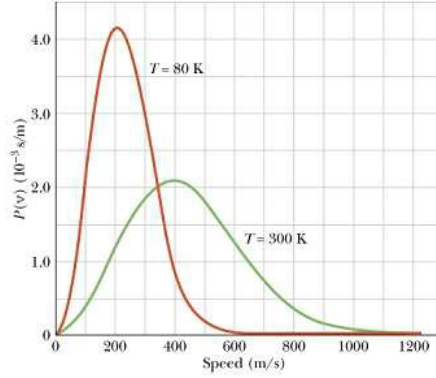
If we are only interested in the distribution for the molecular speed  $v = \sqrt{v_x^2 + v_y^2 + v_z^2}$ , the probability of finding a molecule with speed in the range of  $(v, v + dv)$  is defined to be  $P(v) dv$ . The range of  $(v, v + dv)$  for the speed is actually the region between two spherical shell of radii  $v$  and  $v + dv$  in the Cartesian space of  $\vec{v} = (v_x, v_y, v_z)$ . This spherical region occupies a volume of  $4\pi v^2 dv$  and we have

$$\begin{aligned} P(v) dv &= P(v_x, v_y, v_z) dv_x dv_y dv_z = 4\pi v^2 P(v_x, v_y, v_z) dv \\ &= 4\pi \left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v^2 e^{-\frac{Mv^2}{2RT}} dv \end{aligned}$$

Thus,

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

In this equation  $M$  is the molar mass and  $v$  is the molecular speed.



The product  $P(v)dv$  gives the fraction of the molecules with speed between  $v$  and  $v + dv$ . The integral  $\int_0^\infty P(v)dv$  gives the fraction of molecules with speeds between 0 and  $\infty$ . Thus the integral must be equal to 1. Integral  $\int_{v_1}^{v_2} P(v)dv$  gives the fraction of molecules with speeds between  $v_1$  and  $v_2$ .

### 19.5.1 Average, RMS, and most probable speeds

For (4), if the variable integration  $s$  is changed to  $v$ , we get

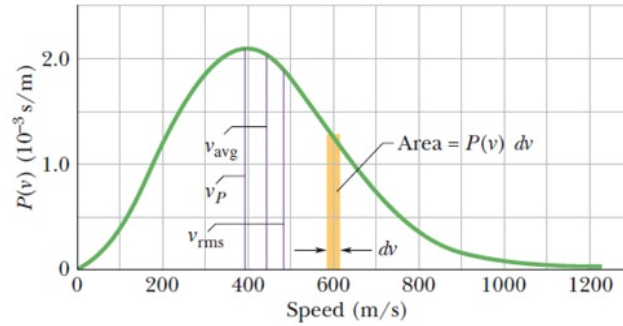
$$\int_{-\infty}^{\infty} e^{-\alpha v^2} dv = \sqrt{\frac{\pi}{\alpha}} \quad (6)$$

Taking the derivative with respect to  $\alpha$  for the above identity, we get

$$\int_{-\infty}^{\infty} v^2 e^{-\alpha v^2} dv = -\frac{\partial}{\partial \alpha} \int_{-\infty}^{\infty} e^{-\alpha v^2} dv = -\frac{\partial}{\partial \alpha} \sqrt{\frac{\pi}{\alpha}} = \frac{1}{2} \frac{\sqrt{\pi}}{\alpha^{\frac{3}{2}}} \quad (7)$$

Similarly,

$$\int_{-\infty}^{\infty} v^4 e^{-\alpha v^2} dv = \left(-\frac{\partial}{\partial \alpha}\right)^2 \int_{-\infty}^{\infty} e^{-\alpha v^2} dv = -\frac{\partial}{\partial \alpha} \left(\frac{1}{2} \frac{\sqrt{\pi}}{\alpha^{\frac{3}{2}}}\right) = \frac{3}{4} \frac{\sqrt{\pi}}{\alpha^{\frac{5}{2}}} \quad (8)$$



The average speed of the molecules is given by the integral:

$$\begin{aligned}
v_{avg} &= \int_0^\infty v P(v) dv = 4\pi \left( \frac{M}{2\pi RT} \right)^{\frac{3}{2}} \int_0^\infty v^3 e^{-\frac{Mv^2}{2RT}} dv \\
&= 2\pi \left( \frac{M}{2\pi RT} \right)^{\frac{3}{2}} \int_0^\infty v^2 e^{-\frac{M}{2RT} v^2} dv^2 = 2\pi \left( \frac{M}{2\pi RT} \right)^{\frac{3}{2}} \frac{1}{\left( \frac{M}{2RT} \right)^2} \\
&= 2\pi \left( \frac{1}{\pi} \right)^{\frac{3}{2}} \frac{1}{\sqrt{\frac{M}{2RT}}} = \sqrt{\frac{8RT}{\pi M}} \text{ (average speed)}
\end{aligned}$$

where we have utilized the integral

$$\int_0^\infty x e^{-\alpha x} dx = -\frac{\partial}{\partial \alpha} \int_0^\infty e^{-\alpha x} dx = -\frac{\partial}{\partial \alpha} \left( \frac{1}{\alpha} \right) = \frac{1}{\alpha^2}$$

The average of the square of the speed is given by the integral:

$$\begin{aligned}
(v^2)_{avg} &= \int_0^\infty v^2 P(v) dv = 4\pi \left( \frac{M}{2\pi RT} \right)^{\frac{3}{2}} \int_0^\infty v^4 e^{-\frac{Mv^2}{2RT}} dv \\
&= 4\pi \left( \frac{M}{2\pi RT} \right)^{\frac{3}{2}} \frac{3}{8} \frac{\sqrt{\pi}}{\left( \frac{M}{2RT} \right)^{\frac{5}{2}}} = \frac{3RT}{M}
\end{aligned}$$

The *root – mean – square* speed

$$v_{rms} = \sqrt{(v^2)_{avg}} = \sqrt{\frac{3RT}{M}} \text{ (rms speed)}$$

in agreement with the results we got before. The most probable speed  $v_p$  is the speed at which  $P(v)$  has a maximum.

$$\frac{dP(v)}{dv} \Big|_{v=v_p} = 0$$

$$\frac{d \left( v^2 e^{-\frac{Mv^2}{2RT}} \right)}{dv} \Big|_{v=v_p} = 2v \left( e^{-\frac{Mv^2}{2RT}} - \frac{M}{2RT} v^2 e^{-\frac{Mv^2}{2RT}} \right) \Big|_{v=v_p} = 0$$

So we have

$$v_p = \sqrt{\frac{2RT}{M}} \text{ (most probable speed)}$$

### 19.5.2 Optional: average relative speed

$$\begin{aligned}
\langle v_{rel} \rangle &= \left\langle \sqrt{(v_{1x} - v_{2x})^2 + (v_{1y} - v_{2y})^2 + (v_{1z} - v_{2z})^2} \right\rangle \\
&= \int \sqrt{(v_{1x} - v_{2x})^2 + (v_{1y} - v_{2y})^2 + (v_{1z} - v_{2z})^2} \\
&\quad \times P(v_{1x}, v_{1y}, v_{1z}) P(v_{2x}, v_{2y}, v_{2z}) dv_{1x} dv_{1y} dv_{1z} dv_{2x} dv_{2y} dv_{2z} \\
&= \left( \frac{m}{2\pi kT} \right)^3 \int \sqrt{(v_{1x} - v_{2x})^2 + (v_{1y} - v_{2y})^2 + (v_{1z} - v_{2z})^2} \\
&\quad \times e^{-\frac{m}{2kT}(v_{1x}^2 + v_{1y}^2 + v_{1z}^2 + v_{2x}^2 + v_{2y}^2 + v_{2z}^2)} dv_{1x} dv_{1y} dv_{1z} dv_{2x} dv_{2y} dv_{2z}
\end{aligned}$$

Let

$$\begin{aligned}
v_{+x} &= \frac{v_{1x} + v_{2x}}{\sqrt{2}}, v_{+y} = \frac{v_{1y} + v_{2y}}{\sqrt{2}}, v_{+z} = \frac{v_{1z} + v_{2z}}{\sqrt{2}} \\
v_{-x} &= \frac{v_{1x} - v_{2x}}{\sqrt{2}}, v_{-y} = \frac{v_{1y} - v_{2y}}{\sqrt{2}}, v_{-z} = \frac{v_{1z} - v_{2z}}{\sqrt{2}}
\end{aligned}$$

we then have (Jacobian)

$$dv_{1x} dv_{1y} dv_{1z} dv_{2x} dv_{2y} dv_{2z} = dv_{+x} dv_{+y} dv_{+z} dv_{-x} dv_{-y} dv_{-z}$$

and

$$\begin{aligned}
\langle v_{rel} \rangle &= \sqrt{2} \left( \frac{m}{2\pi kT} \right)^3 \int \sqrt{v_{-x}^2 + v_{-y}^2 + v_{-z}^2} \\
&\quad \times e^{-\frac{m}{2kT}(v_{+x}^2 + v_{+y}^2 + v_{+z}^2 + v_{-x}^2 + v_{-y}^2 + v_{-z}^2)} dv_{+x} dv_{+y} dv_{+z} dv_{-x} dv_{-y} dv_{-z} \\
&= \sqrt{2} \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int \sqrt{v_{-x}^2 + v_{-y}^2 + v_{-z}^2} e^{-\frac{m}{2kT}(v_{-x}^2 + v_{-y}^2 + v_{-z}^2)} dv_{-x} dv_{-y} dv_{-z} \\
&= \sqrt{2} v_{avg} = \sqrt{2} \sqrt{\frac{8RT}{\pi M}}
\end{aligned}$$

## 19.6 The Molar Specific Heats of an Ideal Gas

### 19.6.1 Internal energy of an ideal gas

Consider a monatomic gas such as He, Ar, or Kr. In this case the internal energy  $E_{int}$  of the gas is the sum of the translational kinetic energies of the

constituent atoms. The average translational kinetic energy of a single atom is given by the equation:

$$K_{avg} = \frac{3kT}{2}$$

A gas sample of  $n$  moles contains  $N = nN_A$  atoms. The internal energy of the gas

$$E_{int} = NK_{avg} = \frac{3}{2}nN_AkT = \frac{3}{2}nRT$$

The equation above is expressing the following important result:

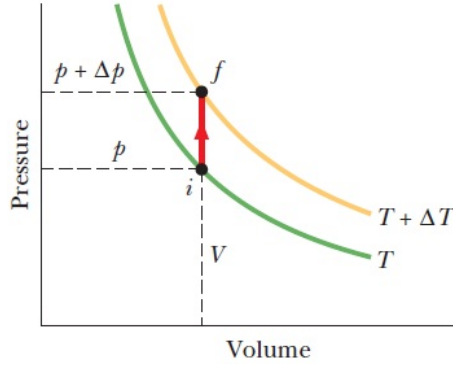
The internal energy  $E_{int}$  of an ideal gas is a function of gas temperature only; it does not depend on any other parameter.

### 19.6.2 Molar specific heat $C_V$ at constant volume

Consider  $n$  moles of an ideal gas at pressure  $p$  and temperature  $T$ . The gas volume is fixed at  $V$ . These parameters define the initial state of the gas. A small heat quantity  $Q$  is added from the reservoir that changes the temperature to  $T + \Delta T$  and the pressure to  $p + \Delta p$  and brings the system to its final state. The heat

$$Q = nC_V\Delta T$$

The constant  $C_V$  is called the molar specific heat at constant volume.



From the first law of thermodynamics we have:

$$Q = \Delta E_{int} + W$$

$$W = p\Delta V = 0$$

Thus

$$Q = \Delta E_{int} = nC_V \Delta T \rightarrow C_V = \frac{\Delta E_{int}}{n\Delta T}$$

$$E_{int} = \frac{3nRT}{2} \rightarrow \Delta E_{int} = \frac{3nR\Delta T}{2} \rightarrow C_V = \frac{3R}{2}$$

We can write the internal energy of the gas in the following form:

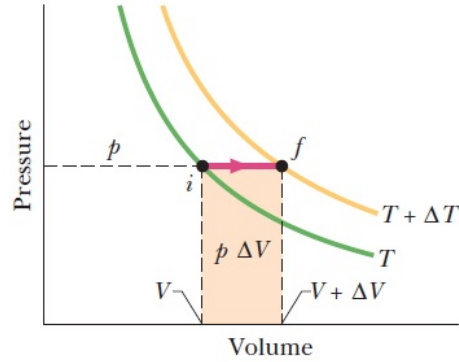
$$E_{int} = nC_V T \rightarrow \Delta E_{int} = nC_V \Delta T$$

### 19.6.3 Molar specific heat $C_p$ at constant pressure

We assume that we add a heat amount  $Q$  to the gas and change its temperature from  $T$  to  $T + \Delta T$  and its volume from  $V$  to  $V + \Delta V$  while keeping the pressure constant at  $p$ . The heat

$$Q = nC_p \Delta T$$

The constant  $C_p$  is called molar specific heat at constant pressure.



The first law of thermodynamics gives:

$$Q = W + \Delta E_{int} \rightarrow nC_p \Delta T = p\Delta V + nC_V \Delta T$$

Using the law of ideal gases  $pV = nRT$  we get:

$$p\Delta V = nR\Delta T \rightarrow nC_p \Delta T = nR\Delta T + nC_V \Delta T$$

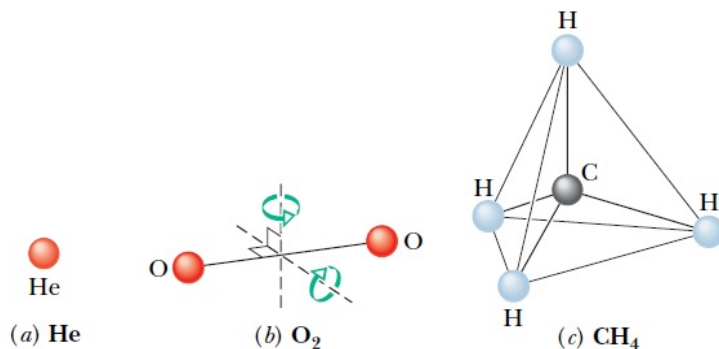
Thus:

$$C_p = C_V + R$$

## 19.7 Degrees of Freedom and Molar Specific Heats

The equation  $C_V = \frac{3R}{2}$  agrees with the experimental data of monatomic gases but fails for diatomic and polyatomic gases. The reason is that for diatomic and polyatomic molecules have more complex motions than the simple translational motion we assumed for monatomic gases. The former can have rotational motion about 2 orthogonal axes and also oscillatory motion about the equilibrium position. To account for these effects Maxwell introduced the theorem of equipartition of energy that states:

Every type of molecule has  $f$  degrees of freedom which defined as independent ways in which the molecule can store energy. Each degree of freedom has an average energy  $\frac{kT}{2}$  per molecule or  $\frac{RT}{2}$  per mole.



The corresponding molar specific heat is:

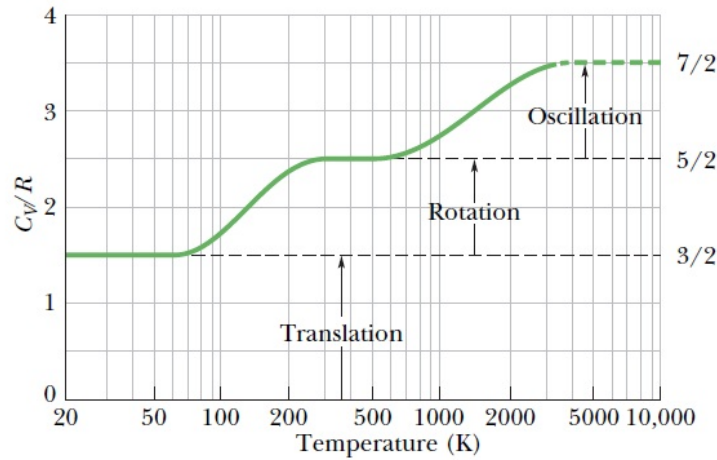
$$C_V = \frac{fR}{2}$$

where  $f = 3$  for monatomic gases,  $f = 5$  for diatomic gases, and  $f = 6$  for polyatomic gases.

### 19.7.1 A Hint of Quantum Theory

We can improve the agreement of kinetic theory with experiment by including the oscillations of the atoms in a gas of diatomic or polyatomic molecules. For example, the two atoms in the  $O_2$  molecule can oscillate toward and away from each other, with the interconnecting bond like a spring. However the experiment shows that such oscillations occur only at a relatively high

temperature of the gas — the motion is "turned on" only when the gas molecules have relatively large energies. Rotational motion is also subject to such "turning on", but at a lower temperature.



**Fig. 19-14**  $C_V/R$  versus temperature for (diatomic) hydrogen gas. Because rotational and oscillatory motions begin at certain energies, only translation is possible at very low temperatures. As the temperature increases, rotational motion can begin. At still higher temperatures, oscillatory motion can begin.

The above figure shows the turning on of rotational motion and oscillatory motion. The ratio  $\frac{C_V}{R}$  for diatomic hydrogen gas ( $H_2$ ) is plotted against temperature, with logarithmic temperature scale to cover several orders of magnitude. Below about 80K, we find that  $\frac{C_V}{R} = 1.5$ . This result implies that only the three translational degrees of freedom of hydrogen are involved in the specific heat.

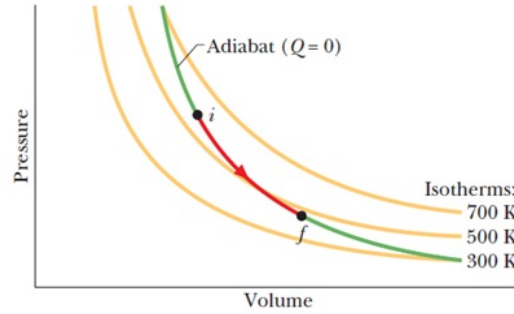
As the temperature increases, the value of  $\frac{C_V}{R}$  gradually increases to 2.5, implies that two additional degrees of freedom have become involved. Quantum theory shows that these degrees of freedom are associated with the rotational motion of the hydrogen molecules and this motion requires a certain minimum amount of energy. At very low temperature (below 80K), the molecules do not have enough energy to rotate. As the temperature increases from 80K, first a few molecules and then more and more obtain enough energy to rotate, and  $\frac{C_V}{R}$  increase, until all of them are rotating and  $\frac{C_V}{R} = 2.5$ .



Similarly, quantum theory shows that oscillatory motion of the molecules requires a certain (higher) minimum amount of energy. This minimum amount is not met until the molecules reach a temperature of about 1000K, more molecules have enough energy to oscillate and  $\frac{C_V}{R}$  increases, until all of them are oscillating and  $\frac{C_V}{R} = 3.5$ .

## 19.8 Adiabatic Expansion of an Ideal Gas

Consider the ideal gas in well-insulated container. When the gas expands no heat is transferred to or from the gas. This process is called adiabatic. Such a process is indicated on the following  $p - V$  diagram by the red line.



The gas starts at an initial pressure  $P_i$  and initial volume  $V_i$ . The corresponding final parameters are  $P_f$  and  $V_f$ . From 1st law of thermodynamics and  $dQ = 0$ , we get

$$dE_{int} = dQ - pdV = -pdV$$

Now substitute  $dE_{int} = nC_V dT$  for an ideal gas. We have

$$nC_V dT = -pdV$$

or

$$nRdT = -\frac{R}{C_V}pdV \quad (9)$$

From the differential of the ideal gas law  $pV = nRT$ , we get

$$d(pV) = Vdp + pdV = nRdT \quad (10)$$

Comparing the above two expressions, we get

$$Vdp + pdV = -\frac{R}{C_V}pdV$$

Diving the whole expression by  $pV$ , we get

$$\frac{dp}{p} + \frac{dV}{V} = -\frac{R}{C_V} \frac{dV}{V}$$

or

$$\frac{dp}{p} + \left(1 + \frac{R}{C_V}\right) \frac{dV}{V} = 0 \rightarrow \frac{dp}{p} + \frac{C_p}{C_V} \frac{dV}{V} = 0$$

Replacing  $\frac{C_p}{C_V}$  with  $\gamma$ ,

$$\gamma = \frac{C_p}{C_V}$$

We then have

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0 \rightarrow d(\ln p + \gamma \ln V) = 0 \rightarrow pV^\gamma = \text{constant}$$

The process is described by the equation:

$$P_i V_i^\gamma = P_f V_f^\gamma$$

Using the ideal gas law we can get the equation:

$$P_i V_i V_i^{\gamma-1} = P_f V_f V_f^{\gamma-1}$$

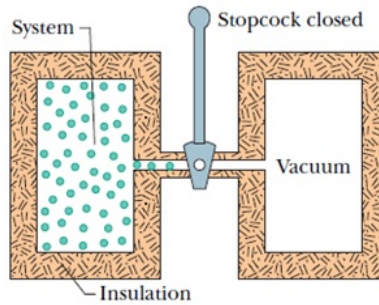
$$nRT_i V_i^{\gamma-1} = nRT_f V_f^{\gamma-1}$$

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \rightarrow T_f = T_i \frac{V_i^{\gamma-1}}{V_f^{\gamma-1}}$$

If  $V_f > V_i$  we have adiabatic expansion and  $T_f < T_i$

If  $V_f < V_i$  we have adiabatic compression and  $T_f > T_i$

### 19.8.1 Free expansion



In a free expansion a gas of initial volume  $V_i$  and initial pressure  $P_i$  is allowed to expand in an empty container so that the final volume is  $V_f$  and the final pressure  $P_f$ . In a free expansion  $\Delta Q = 0$  because the gas container is insulated. Furthermore, since the expansion takes place in vacuum the net work  $\Delta W = 0$ . The first law of thermodynamics predicts that  $\Delta E_{int} = 0$ . Since the gas is assumed to be ideal there is no change in temperature

$$T_i = T_f$$

Using the law of ideal gas, we get the following equation which connects the initial with the final state of the gas:

$$P_i V_i = P_f V_f$$