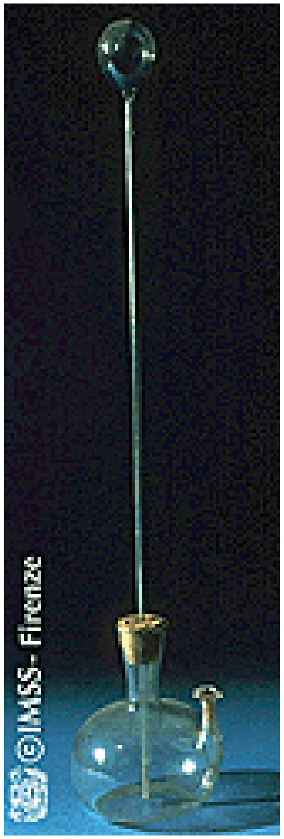
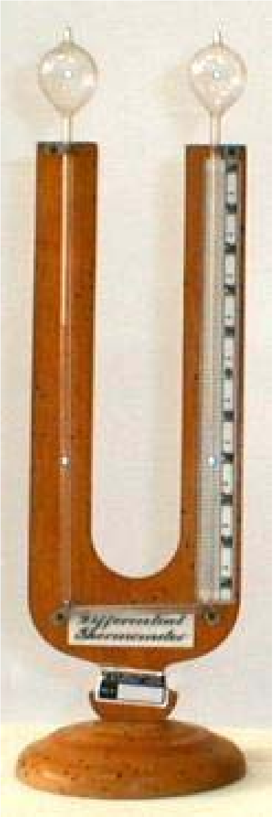
Chapter 14

Kinetic Theory

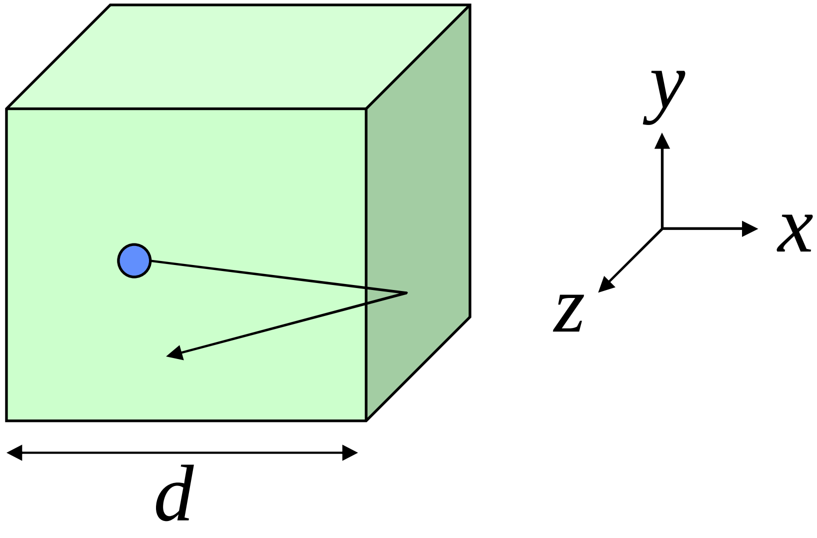


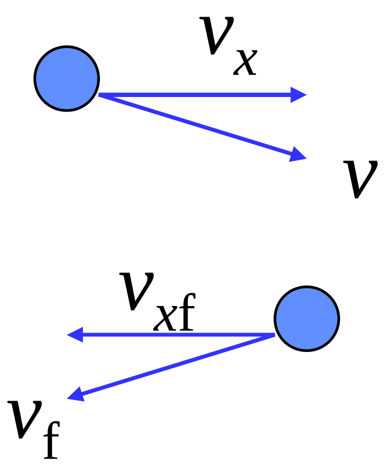


Kinetic Theory of Gases

A remarkable triumph of molecular theory was showing that the macroscopic properties of an ideal gas are related to the molecular properties. This is the kinetic theory of gases.

Consider the "*x*" motion of a gas molecule in a box to determine the gas pressure on the side of the box.





$$v_{xf} = -v_x$$

$$\Delta p_x = m(v_{xf} - v_x) = -2mv_x$$

The average force on the wall is:

$$F'_x = \Delta p_x/\Delta t = -2mv_x/\Delta t$$

The molecule will collide with the right wall in twice the time it takes to traverse the length of the box, *d*. Also, the force on the wall is equal and opposite to the force on the molecule. So the force on the wall is given by

$$F_x = 2mv_x/\Delta t = 2mv_x/(2d/v_x) = mv_x^2/d$$

For the total force, we have to add up the force from every molecule (assuming they all have the same mass):

$F_{xT} = (m/d)\sum v_x^2$

If we note that the average squared velocity $(v_x^2)_{\text{ave}}$ is given by $\langle v_x^2 \rangle = \sum v_x^2/N$ then we see that

$F_{xT} = (Nm/d)\,(v_x^2)_{\text{ave}}$

Also

$\langle v^2 \rangle_{\text{ave}} = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\langle v_x^2 \rangle$

So,

$F_{xT} = (Nm/3d)\,\langle v^2 \rangle$

$P = F/A = (Nm/3d)\langle v^2 \rangle/d^2 = Nm\langle v^2 \rangle/(3V) = nM\langle v^2 \rangle/(3V)$

$P = (2/3)(N/V)\{(1/2)m\langle v^2 \rangle\}$

We have the macroscopic pressure in terms of microscopic velocity.

$PV = (2/3)N\,(1/2)m\langle v^2\rangle$
$NkT = (2/3)N\,(1/2)m\langle v^2\rangle$
$T = (2/3)\,(1/2)m\langle v^2\rangle/k = (2/3k)K_{\mathrm{ave}}$
$K_{\mathrm{ave}} = (3/2)kT$

Temperature is related to the average kinetic energy of the molecules in an ideal gas (and vice versa)!

$\langle v^2\rangle^{1/2} = v_{\mathrm{rms}}$ (rms="root mean square"), so the above equation (for velocity) is usually written as
$3kT = m(v_{\mathrm{rms}})^2$
$v_{\mathrm{rms}} = (3kT/m)^{1/2}$

In general for any molecule, there is an average energy equal to (1/2)kT for each degree of freedom. This is the *Equipartition Theorem*.

Interactive Question

The mass of an oxygen molecule is 16 times that of a hydrogen molecule. At room temperature, the ratio of the rms speed of an oxygen molecule to that of a hydrogen molecule is:

A) 16
B) 4
C) 1
D) 1/4
E) 1/16

Interactive Question

If the molecules in a tank of hydrogen have the same rms speed as the molecules in a tank of oxygen, we may be sure that:

A) the pressures are the same.
B) the hydrogen is at the higher temperature.
C) the hydrogen is at the greater pressure.
D) the temperatures are the same.
E) the oxygen is at the higher temperature.

Monatomic Gas

For N particles of an ideal monatomic gas, the internal energy (U) is given by

$$U = NK_{\mathrm{ave}} = (3/2)\, NkT = (3/2)\, nRT = N_{\mathrm{F}}\, (1/2)\, nRT$$

where N_{F} is the number of degrees of freedom

Using the chapter 14 notation with $c = c_{\mathrm{molar}}$

$$c_{\mathrm{V}} = (1/n)(dQ/dT)_{\mathrm{V}} = (1/n)(dU/dT + dW/dT)_{\mathrm{V}}$$

$$= (1/n)(dU/dT)_{\mathrm{V}}$$

$$= (3/2)R = (N_{\mathrm{F}}/2)\, R$$

$$c_{\mathrm{P}} = (1/n)(dQ/dT)_{\mathrm{P}} = (1/n)(dU/dT + dW/dT)_{\mathrm{P}}$$

$$= (1/n)(dU/dT + P\, dV/dT)_{\mathrm{P}} = c_{\mathrm{V}} + (1/n)(P\, dV/dT)_{\mathrm{P}}$$

$$= c_{\mathrm{V}} + (1/n)(P\, d(nRT/P)/dT)_{\mathrm{P}}$$

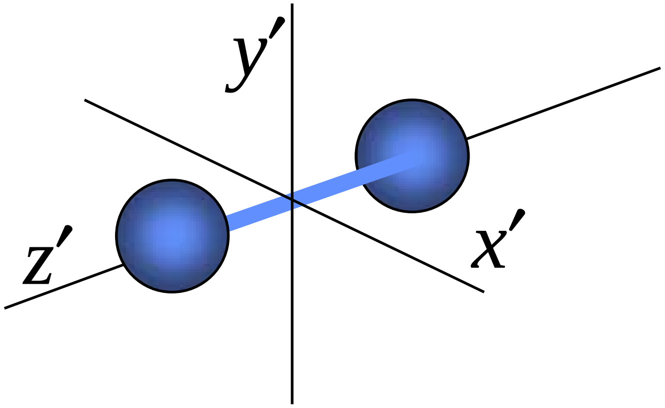
$$= c_{\mathrm{V}} + (1/n)(nR)$$

$$= c_{\mathrm{V}} + R$$

Diatomic Molecules and Degrees of Freedom

$U = N_F(1/2)nRT$

Where N_F is the number of degrees of freedom



$$K = (1/2)mv_x^2 + (1/2)mv_y^2 + (1/2)mv_z^2 + (1/2)I_{x'}\omega_{x'}^2 + (1/2)I_{y'}\omega_{y'}^2$$

$U = (5/2)nRT$

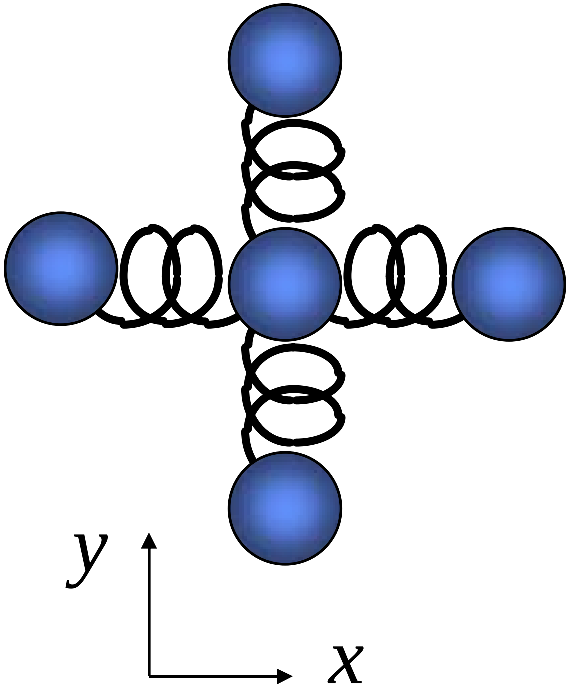
Interactive Question

The pressure of an ideal gas is doubled by halving the volume. The ratio of the new internal energy to the old is:

A) 1/4
B) 1/2
C) 1
D) 2
E) 4

Is temperature only proportional to the average kinetic energy?

Consider a simple model of a solid.



$$E = (1/2)mv_x^2 + (1/2)mv_y^2 + (1/2)mv_z^2 + (1/2)kx^2 + (1/2)ky^2 + (1/2)kz^2$$

$$U = 6\times(1/2)nRT = 3nRT$$

$$c_V = (1/n)\,(dU/dT)_V$$

$$c_V = 3R$$

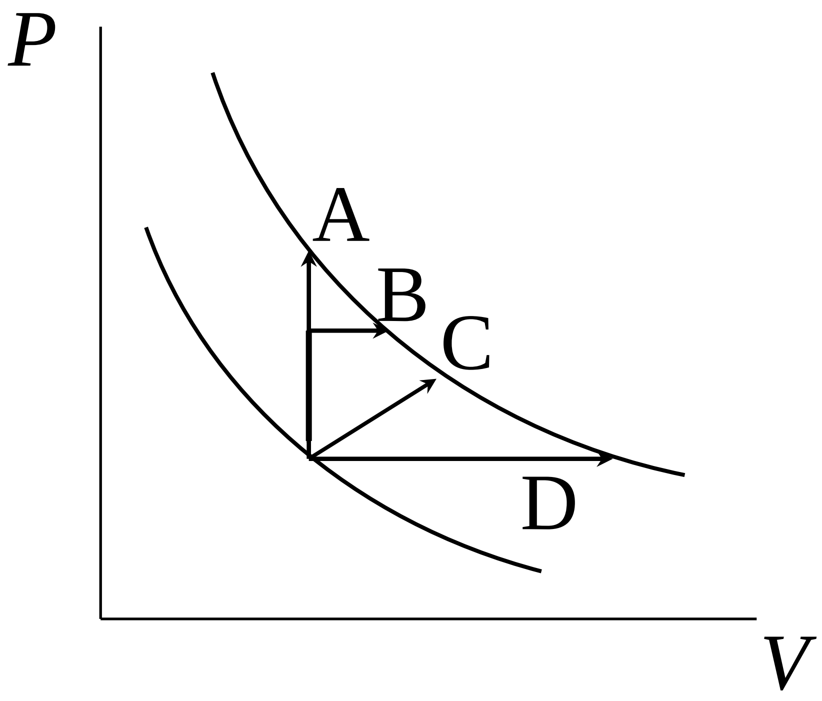
This is the Dulong-Petit Law, first measured in 1819.

Temperature is proportional to the sum of all degrees of freedom of the total energy, including potential energy.

Problem: An ideal gas at a temperature of 300 K and an initial pressure of 2.00×10^5 Pa expands isothermally from a volume of 0.500 m^3 to 1.500 m^3. (a) How much work was done by the gas? (b) What was the change in internal energy of the gas during the process? (c) How much energy was lost to heat in the process?

Interactive Question

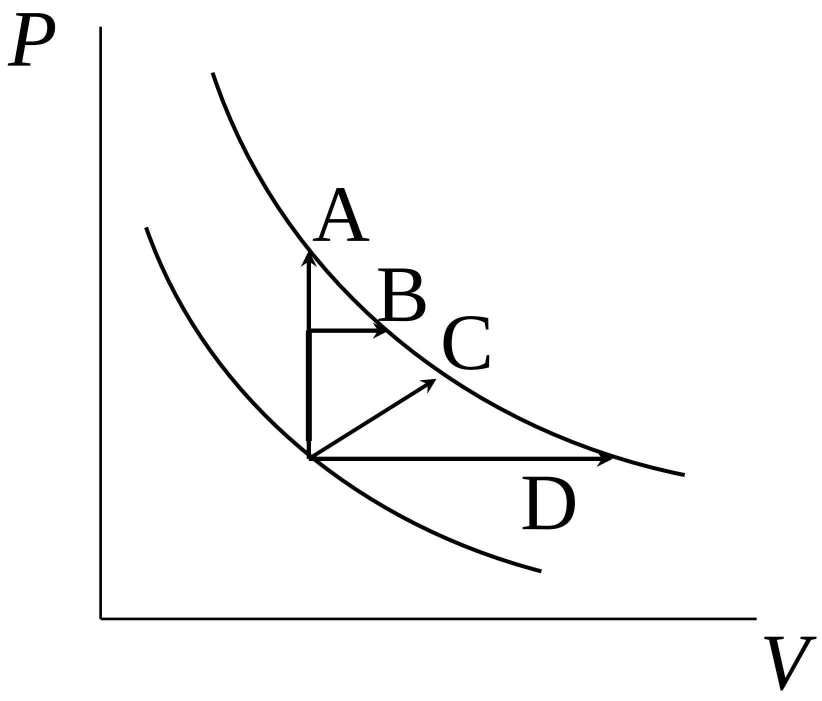
Consider four different methods of moving a system from one isotherm to another. Which has the greatest change in internal energy?



E) None of the Above

Interactive Question

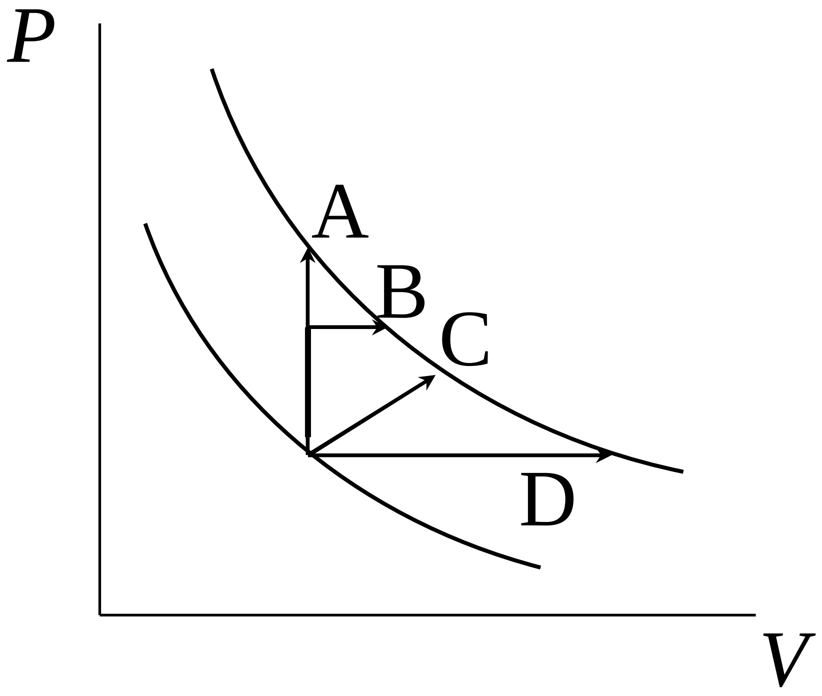
Consider four different methods of moving a system from one isotherm to another. Which has the greatest heat transfer?



E) None of the Above

Interactive Question

Since $Q = C\,\Delta T$, what can you say about C at constant pressure (C_P) compared with C at constant volume (C_V)?



A) $C_P < C_V$
B) $C_P > C_V$
C) $C_P = C_V$
D) Nothing

Problem: How much work is done when an ideal gas undergoes an isobaric expansion from V_1 to V_2?

Adiabatic Expansion of an Ideal Gas

$dU = dQ - dW = -P\,dV$

$nc_V\,dT = -P\,dV$ (1)

To get *dT*, consider an ideal gas:

$PV = nRT$

$P\,dV + V\,dP = nR\,dT$

$dT = (P\,dV + V\,dP)/nR$

Put this back in (1)

$n\,c_V\{(P\,dV + V\,dP)/nR\} = -P\,dV$

$n\,c_V\{(P\,dV + V\,dP)\} = -nRP\,dV$

$(c_V + R)P\,dV + c_V\,V\,dP = 0$

$c_P P\,dV + c_V\,V\,dP = 0$

$(c_P/c_V)\,dV/V + dP/P = 0$

$(c_P/c_V)\int dV/V + \int dP/P = 0$

Adiabatic Expansion of an Ideal Gas (cont.)

$(c_P/c_V) \int dV/V + \int dP/P = 0$

$\gamma \ln V + \ln P = C'$

where $\gamma = c_P/c_V$ and C' is a constant

Since $C \ln A = \ln A^C$, and $\ln A + \ln B = \ln AB$

$\gamma \ln V + \ln P = C'$

$\ln V^\gamma + \ln P = C'$

$\ln PV^\gamma = C'$

$PV^\gamma = e^{C'} = \text{constant}$

This can also be written

$nRTV^\gamma/V = \text{constant}$

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

Note another way to write γ

$$\gamma = c_P/c_V = (c_V + R)/c_V$$

$$= \{(1/2)N_F R + R\}/(1/2)N_F R)$$

$$= \{(1/2)N_F + 1\}/(1/2)N_F)$$

Interactive Question

A system undergoes an adiabatic process in which its internal energy increases by 20 J. Which entry below is correct?

	Heat	Work
A)	None	20 J done on system
B)	None	20 J done by system
C)	20 J removed from system	None
D)	20 J added to system	None
E)	40 J added to system	20 J done by system

Interactive Question

Problem: One mole of oxygen gas (O_2) expands adiabatically from 12 L to 19 L, starting at 310 K. Without doing the actual calculations, how will the final temperature (T_f) compare with the initial temperature (T_i)?

A) $T_i > T_f$
B) $T_i < T_f$
C) $T_i = T_f$

Problem: One mole of oxygen gas (O_2) expands adiabatically from 12 L to 19 L, starting at 310 K. What is the final temperature of this gas?

If the gas in the previous problem undergoes a free expansion starting with a pressure of 2.0 Pa, what is the final pressure of the gas?

Heat Transferred in Various Processes

Isothermal

$Q = \Delta U + W = N_F(1/2)Nk\,\Delta T + W$

$Q = W$

Isobaric

$Q = C_P\,\Delta T = nc_P\,\Delta T$

Isochoric

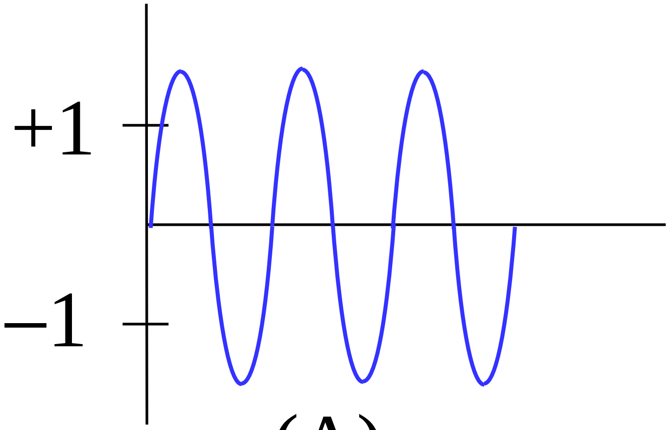
$Q = \Delta U = C_V\,\Delta T = nc_V\,\Delta T$

Adiabatic

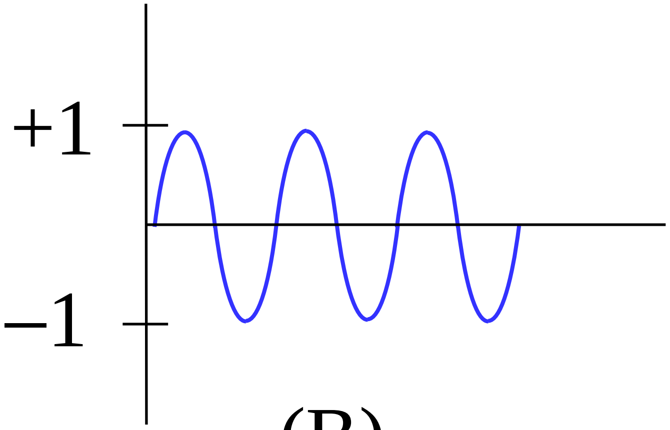
$Q = 0$

Interactive Question

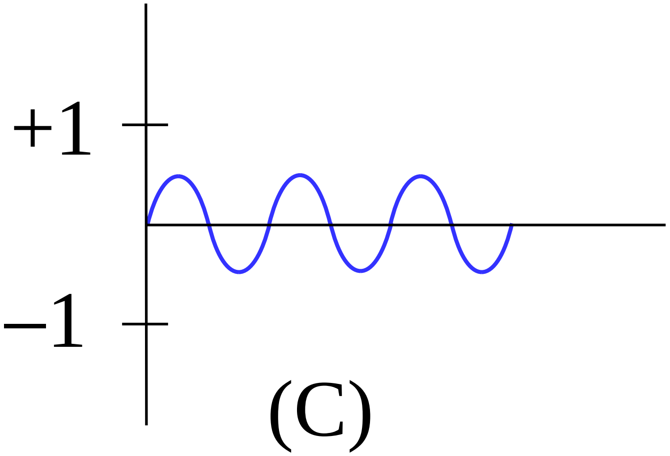
Which plot has the greatest average?



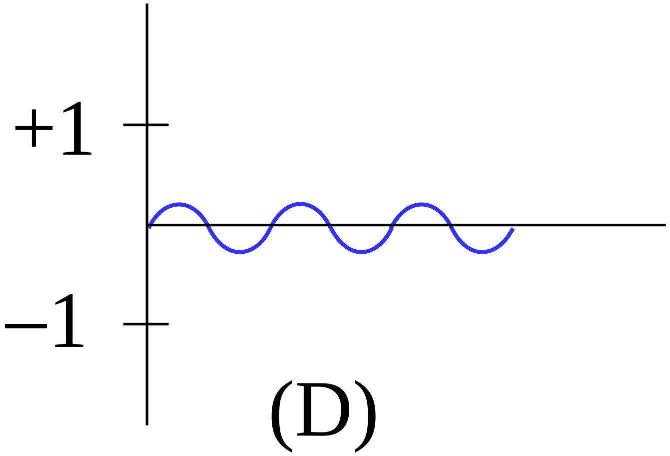
(A)



(B)



(C)



(D)

(E) None of the above

Why might an rms value be more significant than an average value?

Problem: The scores of an exam in an Art class for the 15 students in the class were 95, 89, 97, 72, 93, 83, 81, 69, 89, 83, 72, 89, 77, 82, and 85.

What is (a) the average score, (b) the rms score, and (c) the most probable score

Standard deviation

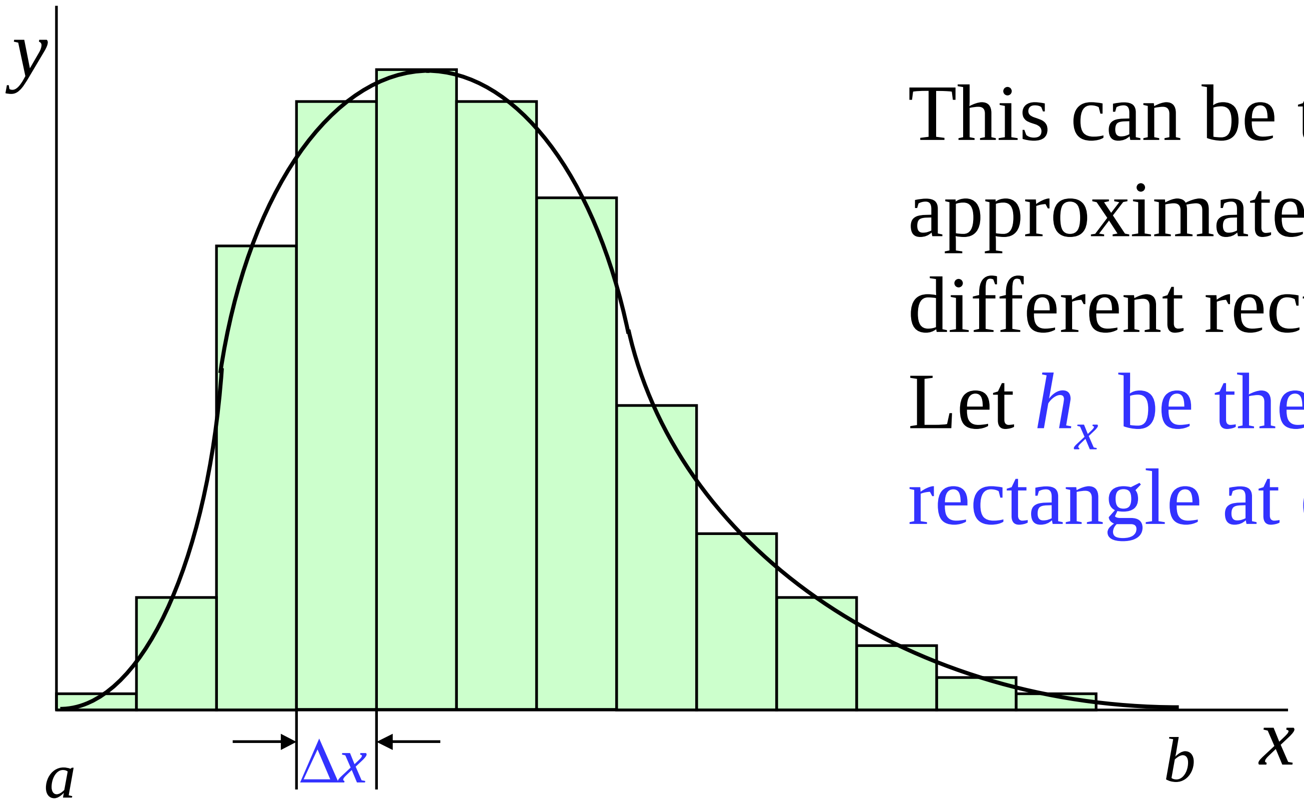
Consider a list of N values from a distribution or experiment, x_i. One way of determining the variation of the values is with the standard deviation, σ.

$$
\begin{aligned}
\sigma^2 &= \{(x_i - x_{\mathrm{av}})^2\}_{\mathrm{av}} = (1/N)\sum^{N}_{i=1} (x_i - x_{\mathrm{av}})^2 \\
&= (1/N)\sum^{N}_{i=1} (x_i^{\,2} - 2x_i x_{\mathrm{av}} + x_{\mathrm{av}}^{\,2}) \\
&= (1/N)\sum^{N}_{i=1} x_i^{\,2} - (1/N)\sum^{N}_{i=1} 2x_i x_{\mathrm{av}} + (1/N)\sum^{N}_{i=1} x_{\mathrm{av}}^{\,2} \\
&= (x^2)_{\mathrm{av}} - 2x_{\mathrm{av}}(1/N)\sum^{N}_{i=1} x_i + (N/N)x_{\mathrm{av}}^{\,2} \\
&= (x^2)_{\mathrm{av}} - 2x_{\mathrm{av}}x_{\mathrm{av}} + x_{\mathrm{av}}^{\,2} \\
&= (x^2)_{\mathrm{av}} - 2x_{\mathrm{av}}^{\,2} + x_{\mathrm{av}}^{\,2} \\
&= (x^2)_{\mathrm{av}} - x_{\mathrm{av}}^{\,2}
\end{aligned}
$$

Suppose the values of x are 5, 10, 15, 20, 25. Then $x_{\mathrm{av}}^{\,2}=225$, and $(x^2)_{\mathrm{av}} = 275$, $\sigma^2 = 50$, $\sigma = 7.1$.

Integrals:

Consider the function $y=h(x)$.



This can be thought of as approximately equal to the different rectangles.

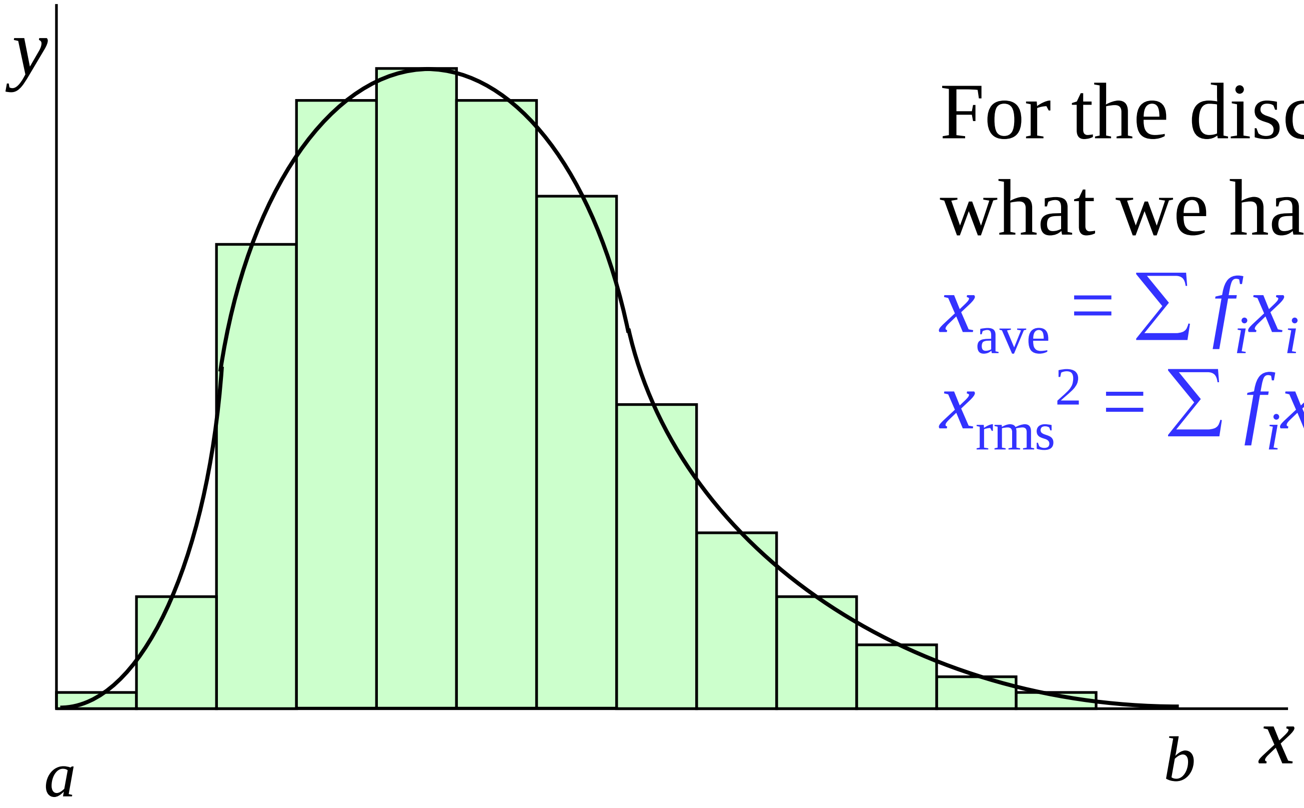
Let h_x be the height of each rectangle at each x value.

The area of the shaded region is given by $A = \sum h_x \Delta x$

The area of the actual function is given by the integral

$A = \int_a^b h(x)\, dx$

Now consider the function $f(x)$ where $f(x)$ is the fraction of the total area in a region dx. $f(x)$ is a probability function.



For the discreet case, this is what we have already done:

$x_{\text{ave}} = \sum f_i x_i$

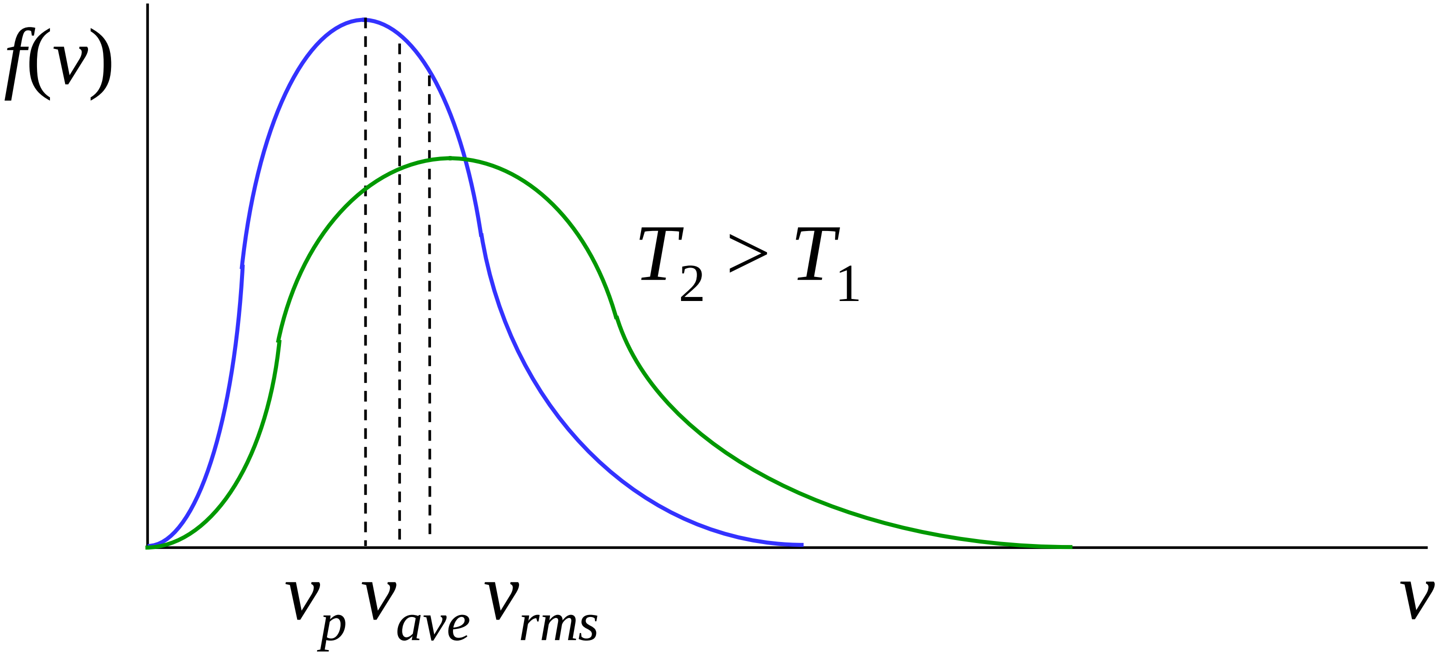
$x_{\text{rms}}{}^2 = \sum f_i x_i^2$

For the continuous case, the average of any function $h(x)$ is given by $h(x)_{\text{ave}} = \int_a^b h(x)\, f(x)\, dx$

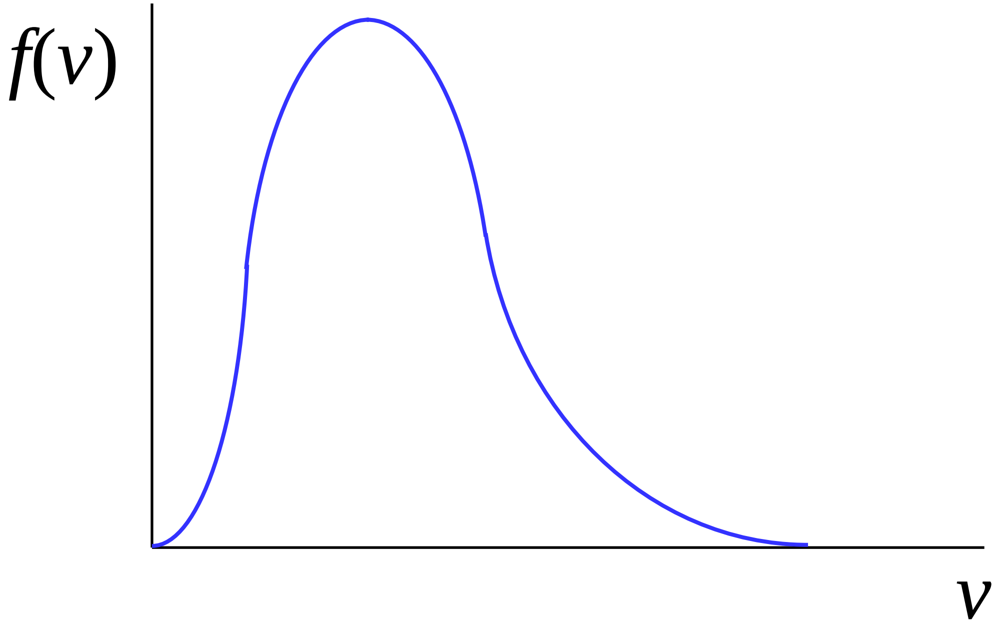
Note that $\int f(x)\, dx = 1.0$

The distribution of molecular speeds in a gas: The Maxwell-Boltzmann distribution

$$f(v) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} v^2 e^{-mv^2/2kT}$$



Evaporation and the Maxwell-Boltzmann Speed Distribution:



$v_{\mathrm{escape}} = 11.2$ km/s

$v_{\mathrm{rms}}(H_2) = 1.93$ km/s

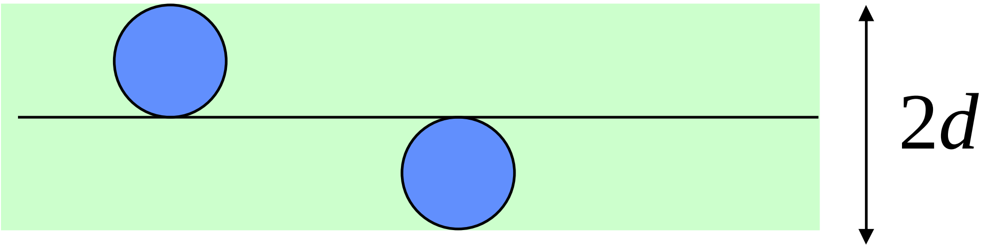
$v_{\mathrm{rms}}(O_2) = 0.5$ km/s

What is the most probable value of the velocity?

What is the rms velocity?

What is the average kinetic energy?

Average Molecular Path Length



$$L = v_{\text{ave}}t$$

The cylinder above has a volume of $\pi d^2\, v_{\text{ave}}t$

The number of molecules in this volume (and the number of collisions in this volume) is $n_V\, \pi d^2\, v_{\text{ave}}t$ where $n_V = N/V$

The mean path length is then

$\lambda = v_{\text{ave}}t/(n_V\, \pi d^2\, v_{\text{ave}}t) = 1/(n_V\, \pi d^2)$

Problem: Estimate the mean-free path of an oxygen molecule at 27° C at a pressure of 1 atm. The oxygen molecule has a radius of about 2.0×10^{-10} m.