Chemistry 232 **Tutorial #4**

1. For O_2 molecules at 300 K, calculate the

   a) mean velocity $\langle v_x \rangle$

   b) root-mean-squared velocity $\langle v_x^2 \rangle^{1/2}$

   c) mean speed $\langle v \rangle$

   d) root-mean-squared speed $\langle v^2 \rangle^{1/2}$

   e) most probable speed v_{mp}

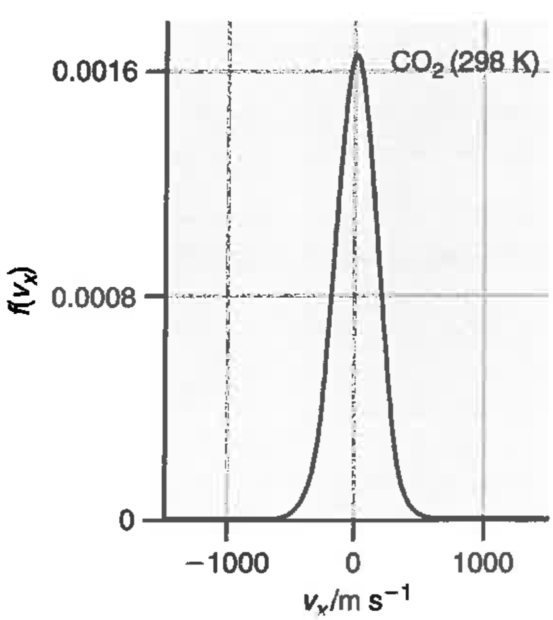
   f) speed of sound (*Data*: $C_{pm}/C_{Vm} = 1.40$)

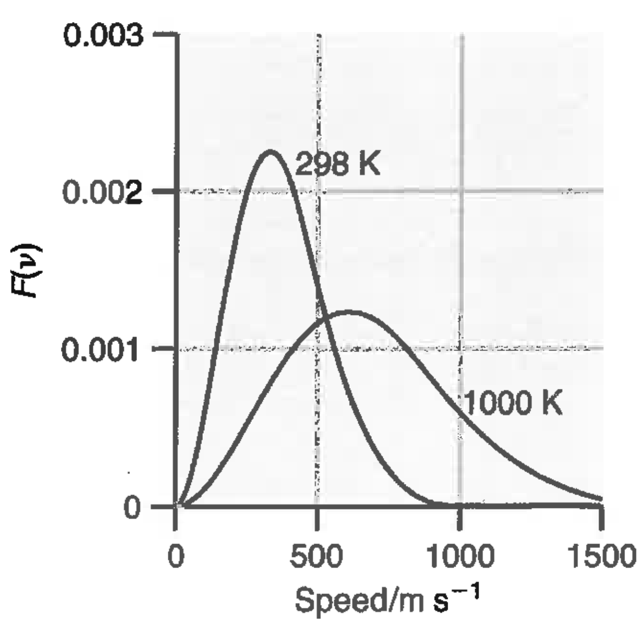
2. Suppose a high-velocity micrometeorite hits the Space Station, cutting a 0.30 mm diameter hole through her hull. Oxygen at 290 K and 0.20 bar starts to leak into outer space.

   a) Calculate the **leak rate** of O_2 in units of mol s^{-1}.

   b) Are the astronauts in danger of suffocating from lack of oxygen? Explain.

3. Molecular velocity distribution functions such as $f(v_x)$ are symmetrical, but the distribution function $F(v)$ for molecular speeds derived from velocity distribution functions are not, as illustrated below. Why?



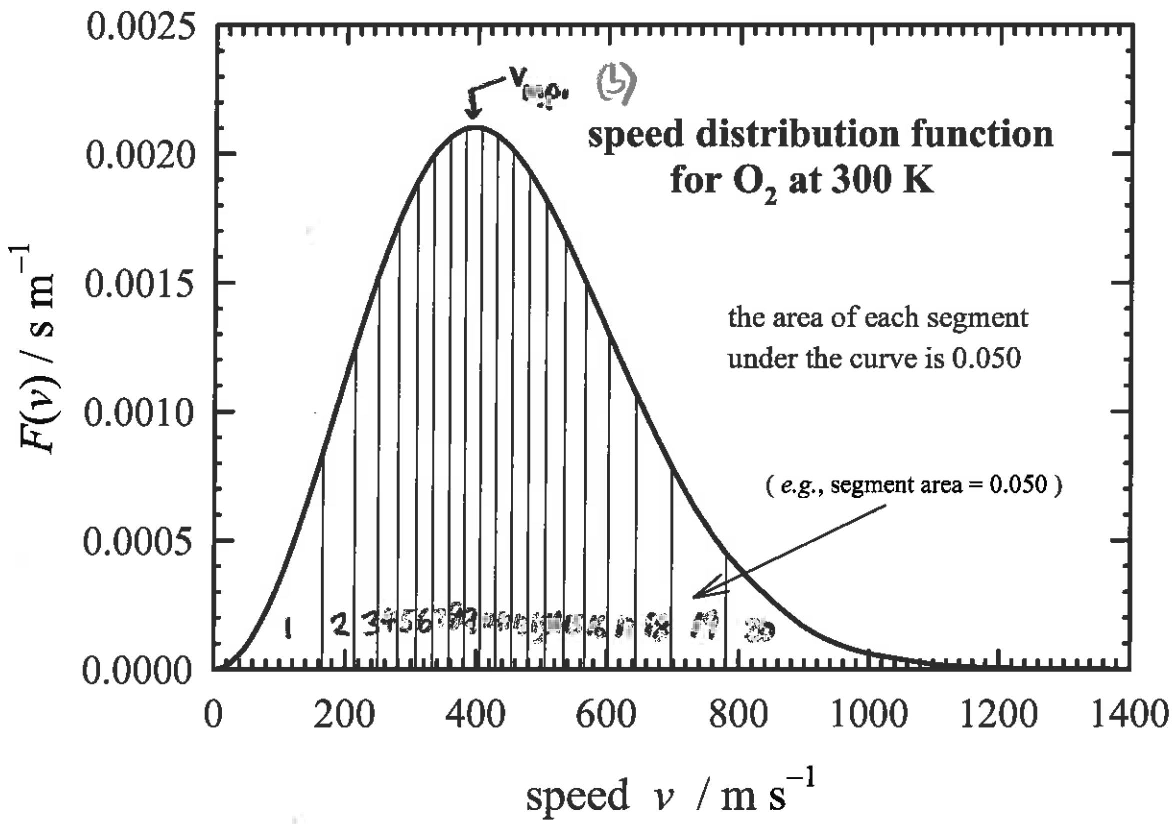


4. Have you ever wondered where the values of R, k. $N_{Avogadro}$, h and other fundamental physical constants come from?

To determine the **molar gas constant** R, the speed of sound in argon gas was measured at the triple point of water (273.16 K, exact by definition). Extrapolation to zero pressure gave 307.8250 m s^{-1} for the speed of sound in the ideal-gas limit $p \rightarrow 0$.

Use $C_{pm}/C_{Vm} = 5/3$ (exact for an ideal monatomic gas) and 39.947735 g mol^{-1} for the atomic weight of argon to calculate a precise value of the molar gas constant R.

5. The diagram below shows the speed distribution function for oxygen molecules at 300 K.



Use the graph to:

a) show that $F(v)$ is a **normalized distribution** (why is this important for calculating probabilities?)

b) give the **most probable speed**

c) estimate the fraction of O_2 molecules with speeds above 600 m s^{-1} (segments 17, 18, 19, 20)

d) calculate the fraction of O_2 molecules with speeds between 400 m s^{-1} and 600 m s^{-1}

e) calculate the **median speed** of O_2 molecules (50 % of the molecules have speeds below the median speed and 50 % have speeds above the median speed.

6. To get some practice calculating probable values, use the **velocity distribution function**

$$f(v_x) = \sqrt{\frac{m}{2\pi kT}}\ \mathrm{e}^{-mv_x^2/2kT}$$

and the **definite integrals** provided below to prove

a) $f(v_x)$ is normalized **b)** $\langle v_x \rangle = 0$ **c)** $\langle v_x^2 \rangle = kT/m$

d) the standard deviation of v_x is $\sqrt{kT/m}$

7. Use the **speed distribution function**

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

and the definite integrals provided below to prove

a) $F(v)$ is normalized **b)** $\langle v \rangle = \sqrt{8kT/\pi m}$ **c)** $\sqrt{\langle v^2 \rangle} = \sqrt{3kT/m}$

Definite Integrals:

$$\int_0^\infty \mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{a}} \qquad \int_{-\infty}^\infty \mathrm{e}^{-ax^2}\,\mathrm{d}x = \sqrt{\frac{\pi}{a}}$$

$$\int_0^\infty x\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{1}{2a} \qquad \int_{-\infty}^\infty x\mathrm{e}^{-ax^2}\,\mathrm{d}x = 0$$

$$\int_0^\infty x^2\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{1}{4}\sqrt{\frac{\pi}{a^3}} \qquad \int_{-\infty}^\infty x^2\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{1}{2}\sqrt{\frac{\pi}{a^3}}$$

$$\int_0^\infty x^3\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{1}{2a^2} \qquad \int_{-\infty}^\infty x^3\mathrm{e}^{-ax^2}\,\mathrm{d}x = 0$$

$$\int_0^\infty x^4\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{3}{8}\sqrt{\frac{\pi}{a^5}} \qquad \int_{-\infty}^\infty x^4\mathrm{e}^{-ax^2}\,\mathrm{d}x = \frac{3}{4}\sqrt{\frac{\pi}{a^5}}$$

Chem 232 <u>Tutorial #4</u>

Q1 O_2 at 300 K molar mass $M = 0.03200 \frac{kg}{mol}$

a) mean velocity $\boxed{\langle v_x \rangle = 0}$ (trick question)

"left" x-velocities just as likely as "right" x-velocities (random molecular velocities)

b) root-mean-square (rms) velocity $\langle v_x^2 \rangle^{1/2}$

$$\sqrt{\langle v_x^2 \rangle} = v_{x(rms)} = \sqrt{\frac{kT}{m}} = \sqrt{\frac{RT}{M}}$$

$$v_{x(rms)} = \sqrt{\frac{(8.314\ J\,K^{-1} mol^{-1})(300\ K)}{0.03200\ kg\ mol^{-1}}} \Leftarrow \left(\text{all SI units}\right)$$

$$\boxed{v_{x(rms)} = 279.2\ m\ s^{-1}}$$

c) mean speed $\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$

$$\langle v \rangle = \sqrt{\frac{8(8.314)(300)}{\pi\ 0.03200}} = \boxed{445.5\ m\ s^{-1}}$$

d) rms speed $= \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$

$$v_{rms} = \sqrt{\frac{3(8.314)300}{0.03200}} = \boxed{483.6\ m\ s^{-1}}$$

e) $v_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2(8.314)300}{0.03200}} = \boxed{394.8\ m\ s^{-1}}$

f) speed of sound $= \sqrt{\frac{C_{pm}}{C_{Vm}} \frac{1}{\rho \kappa_T}} = \sqrt{\gamma \frac{1}{\frac{M}{V_m} \frac{1}{P}}} = \sqrt{\gamma \frac{RT}{M}}$

$$= \sqrt{1.40(8.314)300 / (0.03200)} = \boxed{330.3\ m\ s^{-1}}$$

Q2 O_2 molecules at 0.20 bar and 290 K leak out into a vacuum through a 0.30 mm diameter hole

a) leak rate (molecules per second per unit area):

$$Z_c = \frac{p}{\sqrt{2\pi m k T}} = \frac{p N_{Avogadro}}{\sqrt{2\pi M R T}}$$

in SI units, $p = 20{,}000$ Pa
$M = 0.03200$ kg mol^{-1}

$$Z_c = \frac{(20{,}000)(6.022\times10^{23})}{\sqrt{2\pi(0.03200)\,8.314\,(290)}}$$ all SI unit

$Z_c = 5.47\times10^{26}$ molecules m^{-2} s^{-1}

$$A = \text{hole area} = \pi r^2 = \pi\left(\frac{0.15}{1000}\,m\right)^2 = 7.07\times10^{-8}\,m^2$$

Leak rate through the hole $= Z_c A$

$$= \left(5.47\times10^{26}\,\frac{\text{molecules}}{m^2\,s}\right)\left(7.07\times10^{-8}\,m^2\right)$$

$$= 3.87\times10^{19}\ \text{molecules}\ s^{-1}$$

$$= \frac{3.87\times10^{19}\ \text{molecules}\ s^{-1}}{6.022\times10^{23}\ \text{molecules mol}^{-1}} = 6.42\times10^{-5}\,\frac{mol}{s}$$

b) No immediate danger - very small leak rate - about 5 moles per day, relative to about 20 moles per day consumed per astronaut metabolism

lots of O_2 in reserve

Q3 The molecular velocity distribution is symmetric

$$f(v_x) = f(-v_x)$$

because velocities in the negative x-direction are just as probable as velocities in the positive x-direction (molecular velocities are random)

The molecular speed distribution can't be symmetric in the same sense because speeds (magnitudes of velocities) can never be negative

$$F(v) \overset{?}{=} \cancel{F(-v)}$$ doesn't exist

Also, $F(v)$ is proportional to the Boltzmann exponential factor $e^{-E_{kin}/kT} = e^{-\frac{1}{2}mv^2/kT}$ and to the number of molecules with the same speed (and same Boltzmann factor) – this number is proportional to v^2 (recall the "speed shell" calculation)

result $F(v) \propto (v^2)\, e^{-\frac{1}{2}mv^2/kT}$

the quadratic and exponential factors in v^2 have different symmetry, so $F(v)$ can't be symmetrical, even for positive values

Q4) Use high-precision speed-of-sound data for argon to calculate a precise value of the molar gas constant.

for ideal monatomic gases $c_{sound} = \sqrt{\frac{5}{3}\frac{RT}{M}}$

$$R = \frac{3Mc_{sound}^2}{5T}$$

$$= \frac{3\,(0.039947735 \text{ kg mol}^{-1})(307.8250 \text{ m s}^{-1})^2}{5\,(273.16 \text{ K})}$$

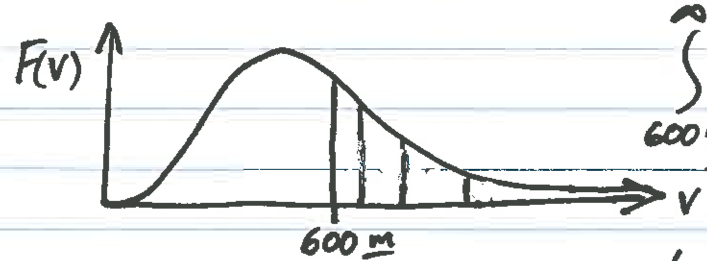
$$R = 8.314461 \text{ J K}^{-1} \text{ mol}^{-1}$$

Q5) a) 20 segments under the curve (count 'em) each with area 0.050 : total area = 20 (0.050) = 1.000

b) the plot of $F(v)$ against v peaks at $v_{mp} \approx 400 \text{ m s}^{-1}$

c) there are ≈ 4.0 segments under the $F(v)$ curve for $v \geq 600 \text{ m s}^{-1}$

See diagram for Q5



$$\int_{600\,\frac{m}{s}}^{\infty} F(v)\,dv \approx 4.0(0.050) = 0.20$$

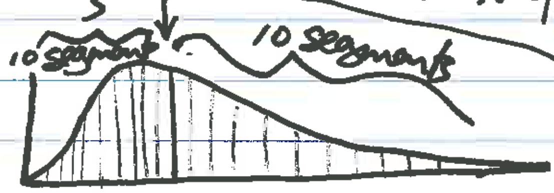
$\approx 20\%$ of the molecules have speeds above $600 \frac{m}{s}$

(segments 17, 18, 19, 20 on diagram)

d) $$\int_{400\,\frac{m}{s}}^{600\,\frac{m}{s}} F(v)\,dv \approx 7.0 \text{ segments} = 7.0\,(0.050) = 0.35$$ segments 10 to 16

$\approx 35\%$ of the molecules have speeds in this range

e)



median speed : 10 segments below, 10 segments above

$v_{median} \approx 430 \text{ m s}^{-1}$

Q6 a) Show $f(v_x)$ is normalized (this is important for calculating probabilities)

$$\int_{-\infty}^{+\infty} f(v_x)\,dv_x = \int_{-\infty}^{\infty}\left(\sqrt{\frac{m}{2\pi kT}}\right) e^{-mv_x^2/2kT}\,dv_x$$

constant

integrate over all possible v_x values, from $-\infty$ to $+\infty$, not 0 to $+\infty$!

$$= \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{\infty} e^{-mv_x^2/2kT}\,dv_x$$

define: $a = \frac{m}{2kT}$

$$= \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{\infty} e^{-av_x^2}\,dv_x$$

$$= \sqrt{\frac{m}{2\pi kT}}\left(\sqrt{\frac{\pi}{a}}\right)$$

from Table of definite integrals

$$= \sqrt{\frac{m}{2\pi kT}}\sqrt{\frac{\pi}{\frac{m}{2kT}}} = 1 \checkmark$$

$f(v_x)$ is normalized

b) show the average x-velocity $\langle v_x \rangle$ is zero

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x)\,dv_x = \int_{-\infty}^{\infty} v_x \sqrt{\frac{m}{2\pi kT}}\, e^{-mv_x^2/2kT}\,dv_x$$

constant

$$= \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{\infty} v_x e^{-mv_x^2/2kT}\,dv_x$$

$a = \frac{m}{2kT}$

$$= \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{\infty} v_x e^{-av_x^2}\,dv_x = \sqrt{\frac{m}{2\pi kT}}\,(0) = 0$$

from Integral Table

(Q6 cont.)

c) show the average squared velocity $\langle v_x^2 \rangle$ is $\frac{kT}{m}$

$$\langle v_x^2 \rangle = \int_{-\infty}^{\infty} v_x^2 f(v_x)\, dv_x$$

$$= \int_{-\infty}^{\infty} v_x^2 \sqrt{\frac{m}{2\pi kT}}\, e^{-mv_x^2/2kT}\, dv_x$$

$$= \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{\infty} v_x^2\, e^{-mv_x^2/2kT}\, dv_x$$

$$a = \frac{m}{2kT}$$

$$= \sqrt{\frac{m}{2\pi kT}} \int_{-\infty}^{\infty} v_x^2\, e^{-av_x^2}\, dv_x$$

Integral Table

$$= \sqrt{\frac{m}{2\pi kT}} \quad \frac{1}{2}\sqrt{\frac{\pi}{a^3}} = \sqrt{\frac{m}{2\pi kT}} \; \frac{1}{2} \left(\frac{2kT}{m}\right)^{3/2} \sqrt{\pi}$$

massive cancellation!

$$= \frac{kT}{m}$$

important result: shows the average translational kinetic energy in one dimension is $\frac{1}{2} m\langle v_x^2 \rangle = \frac{1}{2} kT$

d) standard deviation of v_x = $\sqrt{\text{variance}} = \sqrt{\langle v_x^2 \rangle - \langle v_x \rangle^2}$

standard deviation of v_x: $\sigma_{v_x} = \sqrt{\langle v_x^2 \rangle - 0}$ (part b)

$$\sigma_{v_x} = \sqrt{\langle v_x^2 \rangle} = \sqrt{\frac{kT}{m}}$$

$= v_{x\,rms}$

tells us the "spread" of v_x values increases with T as $\sqrt{T}$ and molecular mass as $\frac{1}{\sqrt{m}}$

Q7 speed distribution function $F(v) = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}$

a) Show $F(v)$ is normalized:

$$\int_0^\infty F(v)\,dv = \int_0^\infty 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\,dv$$

integrate v from 0 to ∞

−∞ not possible

$v \geq 0$ for speeds v

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^2 e^{-mv^2/2kT}\,dv$$

here: $a = \frac{m}{2kT}$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^2 e^{-av^2}\,dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{1}{4}\sqrt{\frac{\pi}{a^3}}$$

from Integral Table

$$= \left(\frac{m}{2kT}\right)^{3/2}\frac{1}{a^{3/2}}$$

$$= \left(\frac{m}{2kT}\right)^{3/2}\frac{1}{\left(\frac{m}{2kT}\right)^{3/2}}$$

$$= 1$$

(Q7 cont.)

b) average speed?

$$\langle v\rangle = \int_0^\infty v\, F(v)\, dv = \int_0^\infty v\, 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-mv^2/2kT}\, dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2kT}\, dv$$

$$a = \frac{m}{2kT}$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^3 e^{-av^2}\, dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{1}{2a^2} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{1}{2}\left(\frac{2kT}{m}\right)^2 = \sqrt{\frac{8kT}{\pi m}}$$

Integral Table

c) root mean-squared speed?

$$\sqrt{\langle v^2\rangle} = \sqrt{\int_0^\infty v^2 F(v)\, dv} = \sqrt{\int_0^\infty v^2\, 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{-\frac{mv^2}{2kT}}\, dv}$$

$$= \sqrt{4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^4 e^{-mv^2/2kT}\, dv}$$

$$= \sqrt{4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^4 e^{-av^2}\, dv} = \sqrt{4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{3}{8}\sqrt{\frac{\pi}{a^5}}}$$

Integral Table

$$= \sqrt{4\left(\frac{m}{2kT}\right)^{3/2}\frac{3}{8}\left(\frac{2kT}{m}\right)^{5/2}} = \sqrt{3\left(\frac{m}{kT}\right)^{3/2}\left(\frac{kT}{m}\right)^{5/2}}$$

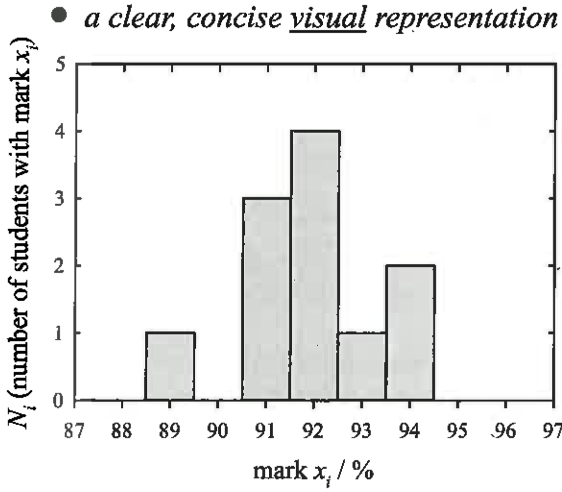
$$\sqrt{\langle v^2\rangle} = \sqrt{3kT/m} = v_{rms}$$

Distribution Functions

- What are they?
- Why are they important?
- How can we use them?

An Example of a Distribution Function

- **histogram plot** of final-exam marks for Chem 232
- number N_i of students with mark x_i plotted against mark x_i
- *a clear, concise visual representation of the data*



a discrete distribution

Why?

N_i and x_i are **not continuous**

$N_i = 0, 1, 2, 3, 4$

$x_i = 89, 91, 92, 93, 94$

What is the average mark?

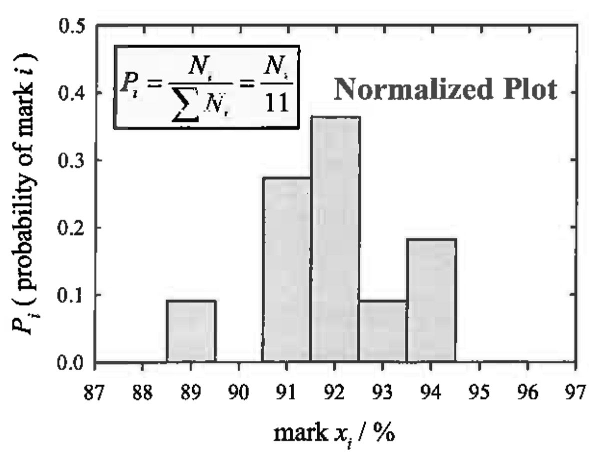
$$\langle x \rangle = \frac{\sum_i N_i x_i}{\sum_i N_i}$$

$$\langle x \rangle = \frac{(1)(89)+(3)(91)+(4)(92)+(1)(93)+(2)(94)}{1+3+4+1+2}$$

$$\boxed{\langle x \rangle = \frac{1101}{11} = 91.90\ \%}$$

another way to calculate the average mark:

- the area under the histogram plot is $\sum N_i = 11$
- Dividing by $\sum N_i = 11$ gives P_i = **the probability of mark x_i**
- the **normalized histogram** is the **mark probability distribution**



Area = 1 under
P_i plotted *vs.* N_i

Why?

The area represents the sum of all possible probabilities.

Calculating average values for a discrete probability distribution

$$\boxed{P_i = \frac{N_i}{\sum N_i}}$$

$$< x > = \sum_i P_i \, x_i$$

$$= P_1x_1 + P_2x_2 + P_3x_3 + P_4x_4 + P_5x_5 + P_6x_6 + P_7x_7 + P_8x_8 + P_9x_9 + P_{10}x_{10} + P_{11}x_{11}$$

$$= \frac{1}{11}89 + \frac{0}{11}90 + \frac{3}{11}91 + \frac{4}{11}92 + \frac{1}{11}93 + \frac{2}{11}94$$

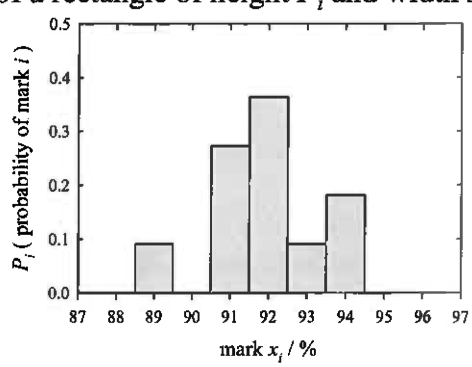
$\boxed{< x > = 91.90}$ average mark

Calculating average values from a discrete probability distribution

$$\boxed{P_i = \frac{N_i}{\sum N_i}}$$

$$< x > = \sum_i P_i \, x_i$$

The probability P_i of mark $x_i = 0, 1, 2, \ldots , 97, 98, 99, 100$ is the area of a rectangle of height P_i and width $\Delta x = 1$.



Average of discrete $x_0,\ x_1,\ x_2, \ldots$ values:

$$\boxed{<x> \ = \ \sum_i P_i\, x_i}$$

What about averages of **continuous** values, such as velocities, speeds, translational kinetic energies, …?

1. Use **probability distribution function** $\boldsymbol{P(x)}$ to give the probability x is between x and $x + \mathrm{d}x$
2. Instead of adding discrete $x_i P_i$ values, integrate $xP(x)\mathrm{d}x$ values:

$$\boxed{<x> \ = \ \int xP(x)\mathrm{d}x}$$

Example: Molecular Speeds

Distribution function:

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

gives the probability $F(v)\mathrm{d}v$ of molecules with speeds in the range from v to $v + \mathrm{d}v$.

Average speed:

$$<v> \ = \ \int_0^\infty vF(v)\mathrm{d}v \ = \ \sqrt{\frac{8kT}{\pi m}}$$