Focus 1: Properties of gases

Perfect gas

Kinetic model

Real gases

Kinetic-molecular theory (KMT)

- A microscopic explanation of gas behavior

Kinetic-molecular theory (KMT)

1. The gas consists of molecules of mass m in ceaseless random motion obeying the laws of classical mechanics.

Kinetic-molecular theory (KMT)

1. The gas consists of molecules of mass m in ceaseless random motion obeying the laws of classical mechanics.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions; they are 'point-like'.

Kinetic-molecular theory (KMT)

1. The gas consists of molecules of mass m in ceaseless random motion obeying the laws of classical mechanics.
2. The size of the molecules is negligible, in the sense that their diameters are much smaller than the average distance travelled between collisions; they are 'point-like'.
3. The molecules interact only through brief elastic collisions.

Relation between pressure and volume: $PV= 1/3\ nMV_{rms}^2$

- Connects microscopic properties of a gas with macroscopic properties

$$pV = \tfrac{1}{3} nMv_{\mathrm{rms}}^2$$

Relation between pressure and volume: PV= 1/3 nMV$_{rms}^2$

Molar mass

$$pV = \tfrac{1}{3} n M v_{\mathrm{rms}}^2$$

No of moles

Root-mean-square speed

$$v_{\mathrm{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \cdots + v_n^2}{n}} = \left(\frac{3RT}{M}\right)^{1/2}$$

Comes from the KMT and relates the macroscopic temperature (T) of a gas to the microscopic average speed of its molecules

Relation between pressure and volume: PV= 1/3 nMV_{rms}^2

Molar mass

$$pV = \tfrac{1}{3} nMv_{\mathrm{rms}}^2$$

No of moles

Root-mean-square speed

Temperature dependence?

$$v_{\mathrm{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \cdots + v_n^2}{n}} = \left(\frac{3RT}{M}\right)^{1/2}$$

Comes from the KMT and relates the macroscopic temperature (T) of a gas to the microscopic average speed of its molecules

Relation between pressure and volume: PV= 1/3 nMV_{rms}^2

Molar mass

$$pV = \tfrac{1}{3} nMv_{\text{rms}}^2$$

No of moles

Root-mean-square speed

$$v_{\text{rms}} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \cdots + v_n^2}{n}} = \left(\frac{3RT}{M}\right)^{1/2}$$

Temperature dependence?

PV = constant (at constant T)

Comes from the KMT and relates the macroscopic temperature (T) of a gas to the microscopic average speed of its molecules

Maxwell-Boltzmann distribution of speeds

Maxwell-Boltzmann distribution of speeds

Molar mass

distribution of speeds

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

Gas constant

temperature

Maxwell-Boltzmann distribution of speeds

Molar mass

distribution of speeds

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

Gas constant

temperature

Boltzmann factor $exp\,(-E/k_B T)$ indicates how likely a system is to occupy a state with energy E.

Maxwell-Boltzmann distribution of speeds

distribution of speeds

Molar mass

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

Gas constant

temperature

Boltzmann factor $exp\ (-E/k_BT)$ indicates how likely a system is to occupy a state with energy E.

R	
8.314 47	J K^{-1} mol^{-1}
8.205 74 × 10^{-2}	dm^3 atm K^{-1} mol^{-1}
8.314 47 × 10^{-2}	dm^3 bar K^{-1} mol^{-1}
8.314 47	Pa m^3 K^{-1} mol^{-1}
62.364	dm^3 Torr K^{-1} mol^{-1}
1.987 21	cal K^{-1} mol^{-1}

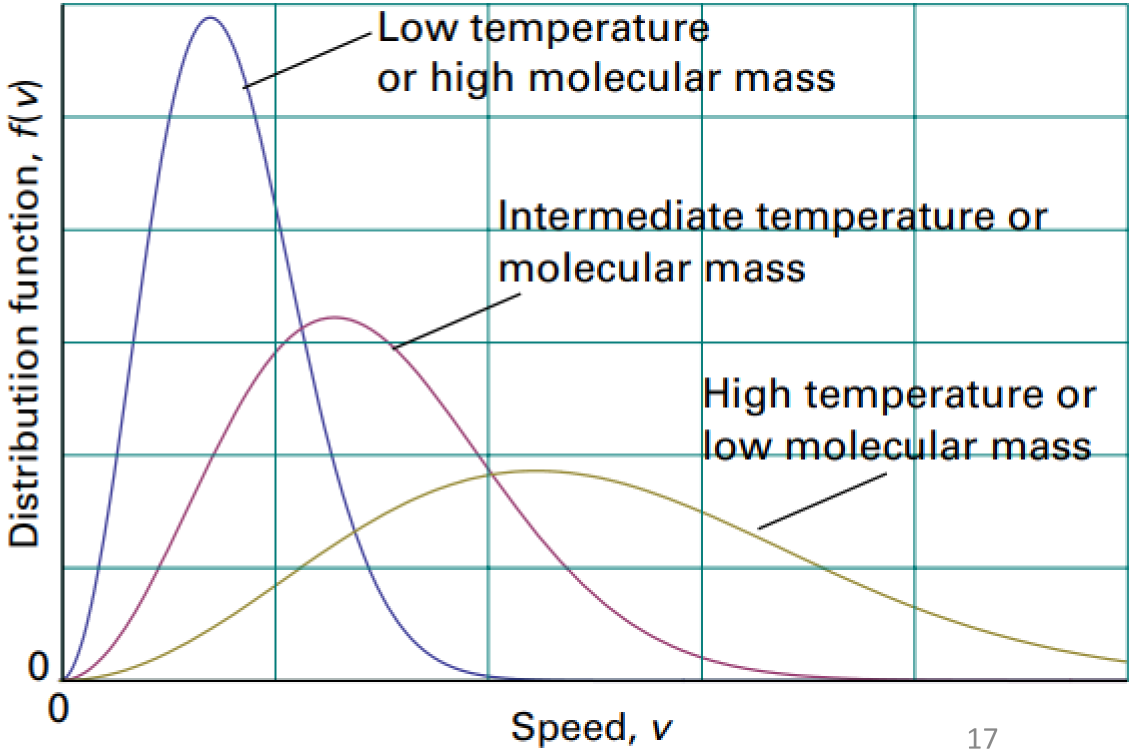
Maxwell-Boltzmann distribution

Molar mass

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

temperature

Distribution of speeds of particles in a gas at different temperatures or for different molecular masses



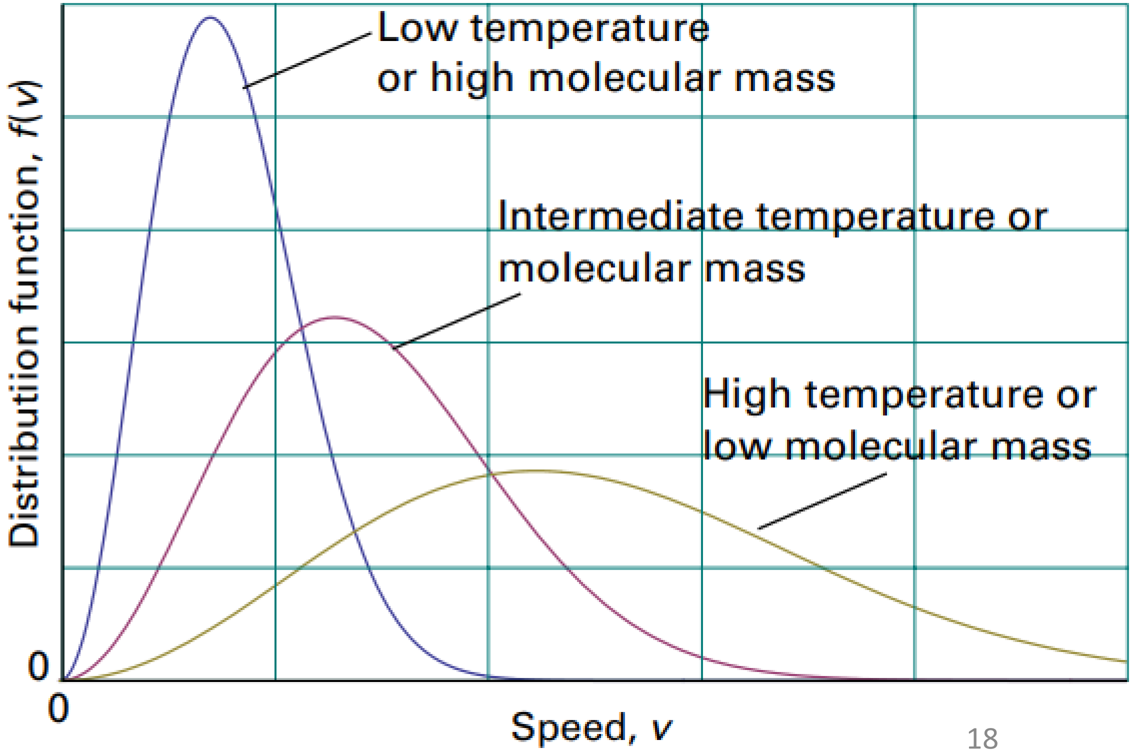
Maxwell-Boltzmann distribution

Molar mass

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

temperature

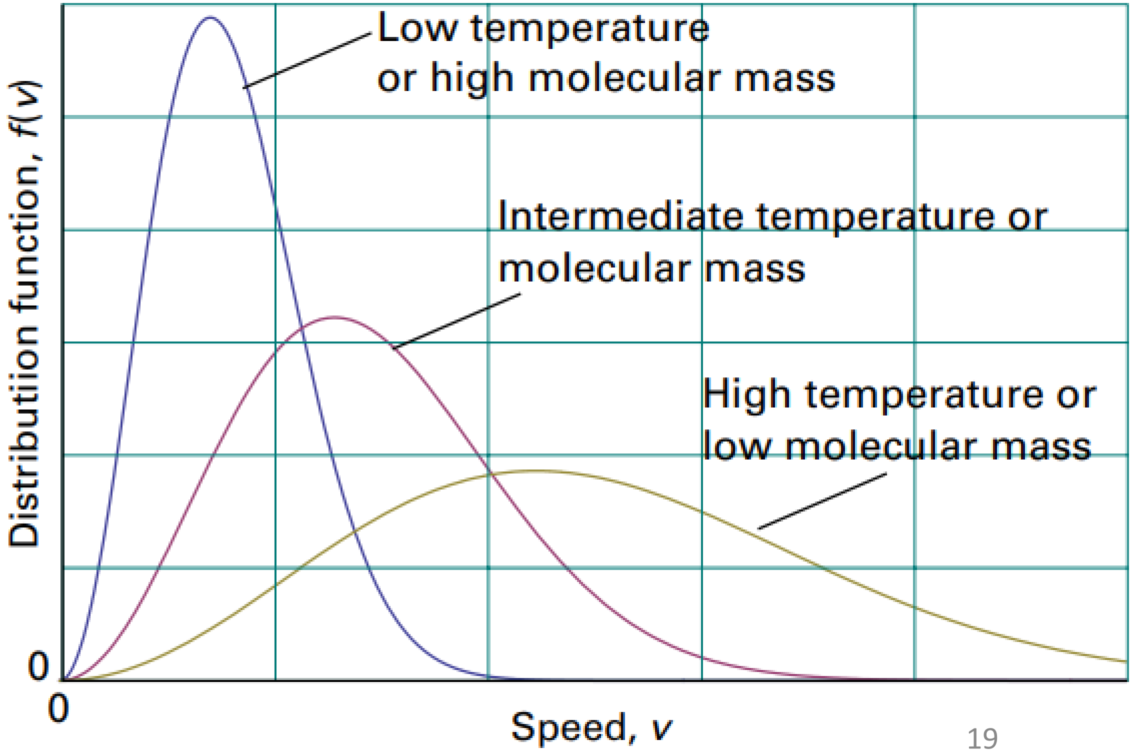
Most probable speed?



Maxwell-Boltzmann distribution

Most probable speed?

Effect of Temperature	**Low Temperature (blue curve)**	- Curve is narrower and peaks at a lower speed.
		- Particles move more slowly on average due to lower kinetic energy.
	High Temperature (yellow curve)	- Curve flattens and shifts to the right, indicating higher speeds.
		- Particles gain more kinetic energy, increasing average speed and range.
Effect of Molecular Mass	**Low Molecular Mass (yellow curve)**	- Particles have higher average speeds and a broader distribution.
		- Distribution is similar to high temperature for lighter molecules.
	High Molecular Mass (blue curve)	- Particles have lower average speeds and a narrower distribution.
		- Heavier particles move more slowly at the same temperature.



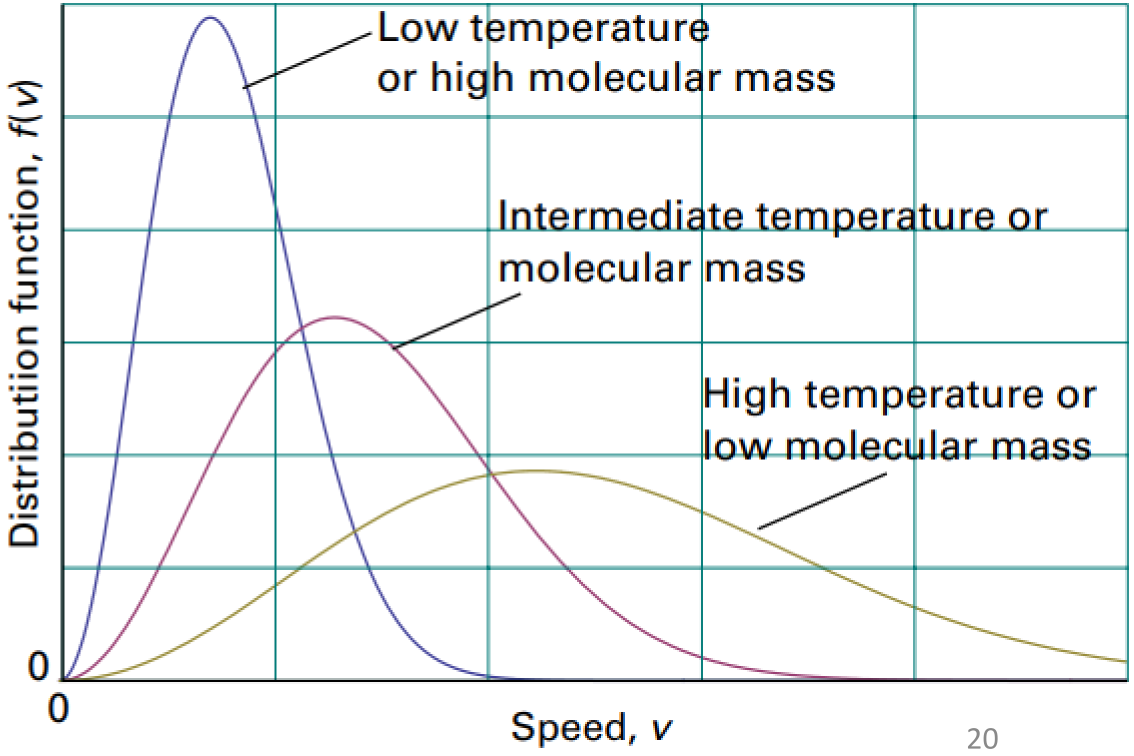
Maxwell-Boltzmann distribution

molecules with speeds in the range v_1 to v_2

$$F(v_1, v_2) = \int_{v_1}^{v_2} f(v)\mathrm{d}v$$

Effect of Temperature	Low Temperature (blue curve)	- Curve is narrower and peaks at a lower speed.
		- Particles move more slowly on average due to lower kinetic energy.
	High Temperature (yellow curve)	- Curve flattens and shifts to the right, indicating higher speeds.
		- Particles gain more kinetic energy, increasing average speed and range.
Effect of Molecular Mass	Low Molecular Mass (yellow curve)	- Particles have higher average speeds and a broader distribution.
		- Distribution is similar to high temperature for lighter molecules.
	High Molecular Mass (blue curve)	- Particles have lower average speeds and a narrower distribution.
		- Heavier particles move more slowly at the same temperature.

Distribution of speeds of particles in a gas at different temperatures or for different molecular masses



Mean speed

molecules with speeds in the range v_1 to v_2 $$F(v_1,v_2)=\int_{v_1}^{v_2} f(v)\mathrm{d}v$$

The average value of v^n $$\langle v^n\rangle=\int_0^{\infty} v^n f(v)\mathrm{d}v$$

- The formula is derived from the Maxwell-Boltzmann distribution of speeds and is used in statistical mechanics to calculate averages of different powers of speed.
- Each possible speed raised to the nth power by its probability density (f(v)) and integrating over all speeds from 0 to ∞.

If $n = 1$, it gives the average speed ($\langle v\rangle$).

If $n = 2$, it gives the mean square speed ($\langle v^2\rangle$).

If $n = 3$, it gives the average of v^3, and so on.

Mean speed

molecules with speeds in the range v_1 to v_2 $\quad F(v_1, v_2) = \int_{v_1}^{v_2} f(v)\mathrm{d}v$

The average value of v^n $\quad \langle v^n \rangle = \int_0^\infty v^n f(v)\mathrm{d}v$

The mean speed $\quad v_{\text{mean}} = \int_0^\infty v f(v)\mathrm{d}v$

Mean speed

molecules with speeds in the range v_1 to v_2 $\quad F(v_1,v_2)=\int_{v_1}^{v_2} f(v)\mathrm{d}v$

The average value of v^n $\quad \langle v^n \rangle = \int_0^{\infty} v^n f(v)\mathrm{d}v$

The mean speed $\quad v_{\text{mean}} = \int_0^{\infty} v f(v)\mathrm{d}v \qquad f(v)=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \mathrm{e}^{-Mv^2/2RT}$

Mean speed

molecules with speeds in the range v_1 to v_2 $F(v_1,v_2)=\int_{v_1}^{v_2} f(v)\mathrm{d}v$

The average value of v^n $\langle v^n\rangle=\int_0^{\infty} v^n f(v)\mathrm{d}v$

The mean speed $v_{\text{mean}}=\int_0^{\infty} v f(v)\mathrm{d}v$ $f(v)=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \mathrm{e}^{-Mv^2/2RT}$

$$v_{\text{mean}}=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^{\infty} v^3 \mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v$$

Mean speed

molecules with speeds in the range v_1 to v_2 $$F(v_1,v_2)=\int_{v_1}^{v_2} f(v)\mathrm{d}v$$

The average value of v^n $$\langle v^n\rangle=\int_0^\infty v^n f(v)\mathrm{d}v$$

The mean speed $$v_{\text{mean}}=\int_0^\infty v f(v)\mathrm{d}v \qquad f(v)=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$$

$$v_{\text{mean}}=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty v^3 e^{-Mv^2/2RT}\,\mathrm{d}v$$

$$=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\times\tfrac{1}{2}\left(\frac{2RT}{M}\right)^2=\left(\frac{8RT}{\pi M}\right)^{1/2}$$

Mean speed

molecules with speeds in the range v_1 to v_2 $\quad F(v_1,v_2)=\int_{v_1}^{v_2} f(v)\mathrm{d}v$

The average value of v^n $\quad \langle v^n\rangle=\int_0^\infty v^n f(v)\mathrm{d}v$

The mean speed $\quad v_{\text{mean}}=\int_0^\infty v f(v)\mathrm{d}v \qquad f(v)=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \mathrm{e}^{-Mv^2/2RT}$

$$v_{\text{mean}}=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty v^3 \mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v$$

$$=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\times\tfrac{1}{2}\left(\frac{2RT}{M}\right)^2=\left(\frac{8RT}{\pi M}\right)^{1/2}$$

From slide 11

$$v_{\text{rms}}=\langle v^2\rangle^{1/2}=\left(\frac{3RT}{M}\right)^{1/2}$$

Mean speed

molecules with speeds in the range v_1 to v_2 $\quad F(v_1,v_2)=\int_{v_1}^{v_2} f(v)\mathrm{d}v$

The average value of v^n $\quad \langle v^n\rangle=\int_0^{\infty} v^n f(v)\mathrm{d}v$

The mean speed $\quad v_{\text{mean}}=\int_0^{\infty} v f(v)\mathrm{d}v \qquad f(v)=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \mathrm{e}^{-Mv^2/2RT}$

$$v_{\text{mean}}=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^{\infty} v^3 \mathrm{e}^{-Mv^2/2RT}\,\mathrm{d}v$$

$$=4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\times\frac{1}{2}\left(\frac{2RT}{M}\right)^{2}=\left(\frac{8RT}{\pi M}\right)^{1/2}$$

From slide 11

$$v_{\text{rms}}=\langle v^2\rangle^{1/2}=\left(\frac{3RT}{M}\right)^{1/2}$$

$$\boxed{v_{\text{mean}}=\left(\frac{8RT}{\pi M}\right)^{1/2}=\left(\frac{8}{3\pi}\right)^{1/2} v_{\text{rms}}}$$

Mean speed of N_2 at 15 ^{O}C?

Calculate V_{mean} of N_2 at 15 ^{O}C

Mean speed of N_2 at 15 ^{O}C?

Calculate V_{mean} of N_2 at 15 ^{O}C

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8}{3\pi}\right)^{1/2} v_{\text{rms}}$$

Mean speed of N_2 at 15 ^{O}C?

Calculate V_{mean} of N_2 at 15 ^{O}C

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$v_{\text{mean}} = \left(\frac{8\times(8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1})\times 288\ \text{K}}{\pi\times(0.028\,02\,\text{kg}\,\text{mol}^{-1})}\right)^{1/2} = 462\ \text{ms}^{-1}$$

Apprx. 1033 mph.

Mean speed of N_2 at 15 ^{O}C?

Calculate V_{mean} of N_2 at 15 ^{O}C

$$v_{\text{mean}} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left(\frac{8}{3\pi}\right)^{1/2} v_{\text{rms}}$$

$$v_{\text{mean}} = \left(\frac{8 \times (8.3145\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}) \times 288\ \text{K}}{\pi \times (0.028\,02\,\text{kg}\,\text{mol}^{-1})}\right)^{1/2} = 462\ \text{ms}^{-1}$$

Most probable speed

$$v_{\mathrm{mp}} = \left(\frac{2RT}{M} \right)^{1/2}$$

Most probable speed

$$v_{\mathrm{mp}} = \left(\frac{2RT}{M} \right)^{1/2}$$

Maxwell-Boltzmann Distribution Function:

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

Set $\frac{df(v)}{dv} = 0$:

Most probable speed

$$v_{\mathrm{mp}} = \left(\frac{2RT}{M}\right)^{1/2} = \left(\frac{2}{3}\right)^{1/2} v_{\mathrm{rms}}$$

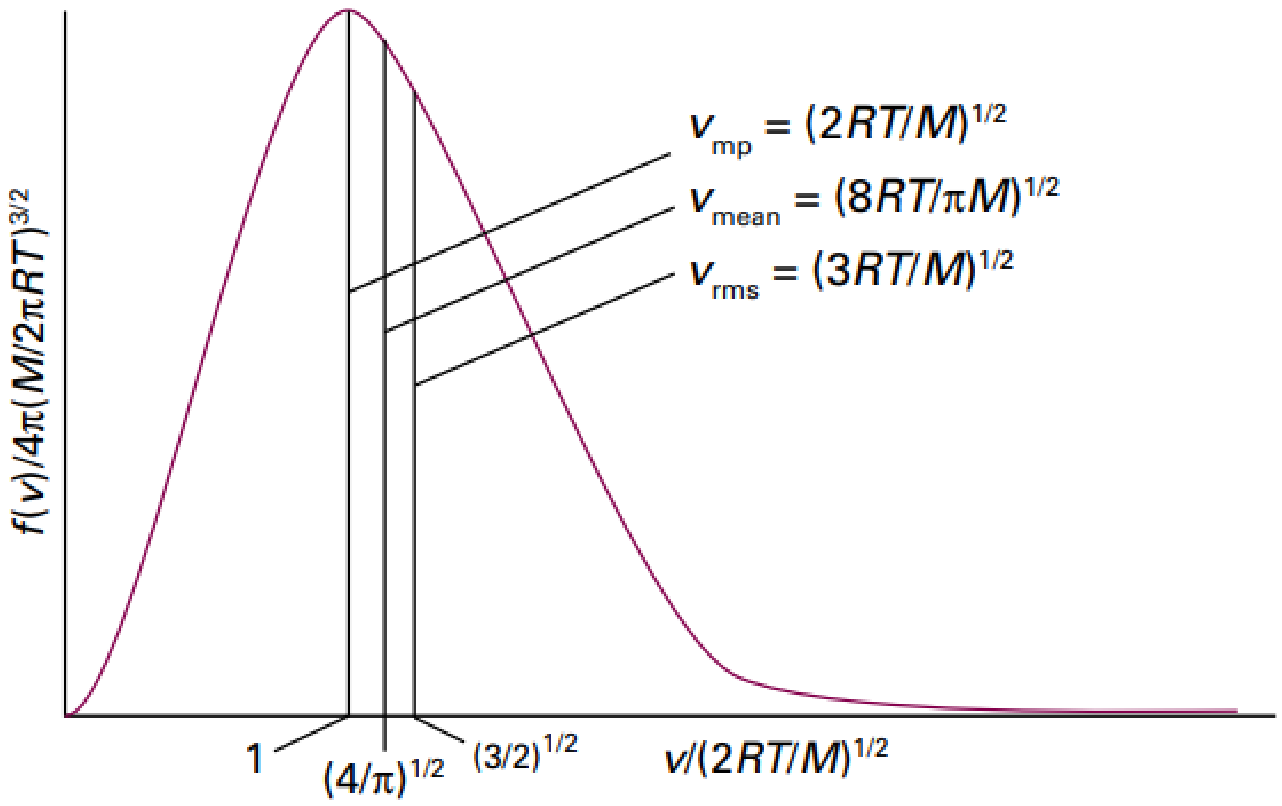
Maxwell-Boltzmann Distribution Function:

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

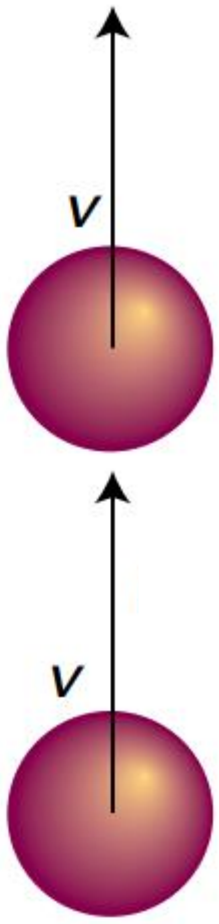
Set $\frac{df(v)}{dv} = 0$:

Vmp, Vmean, and Vrms

A summary of the conclusions that can be deduced from the Maxwell distribution for molecules of molar mass M at a temperature T

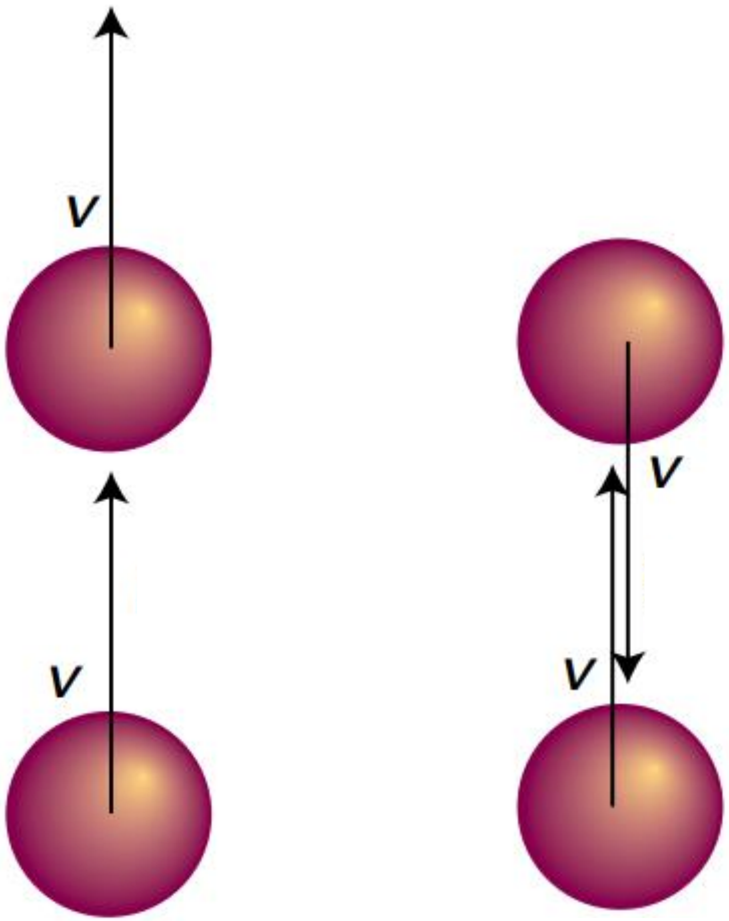


Relative speed of a molecule w.r.t. another



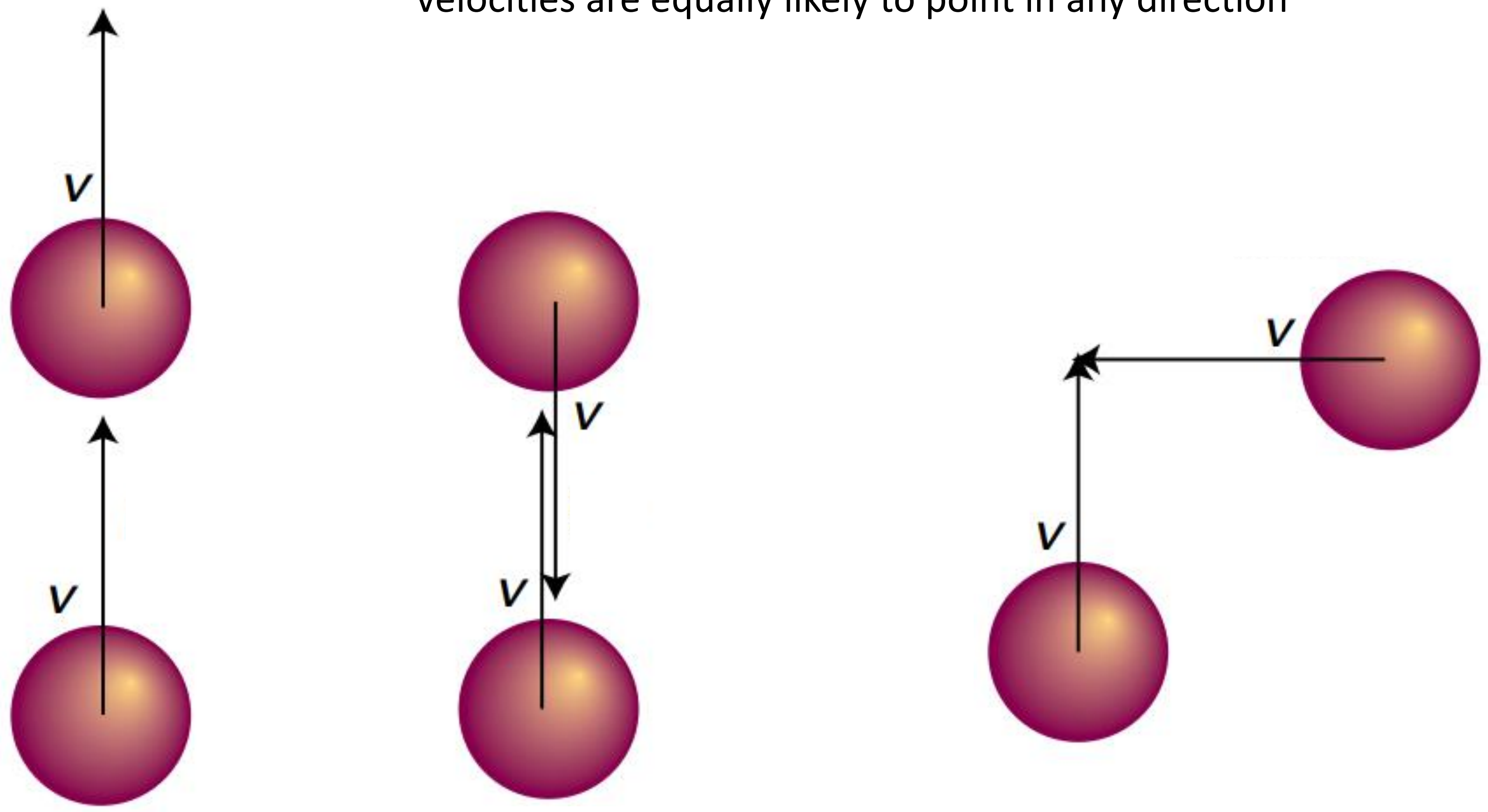
The relative speed between two molecules is the speed of one molecule as observed from the frame of reference of the other molecule.

Relative speed of a molecule w.r.t. another

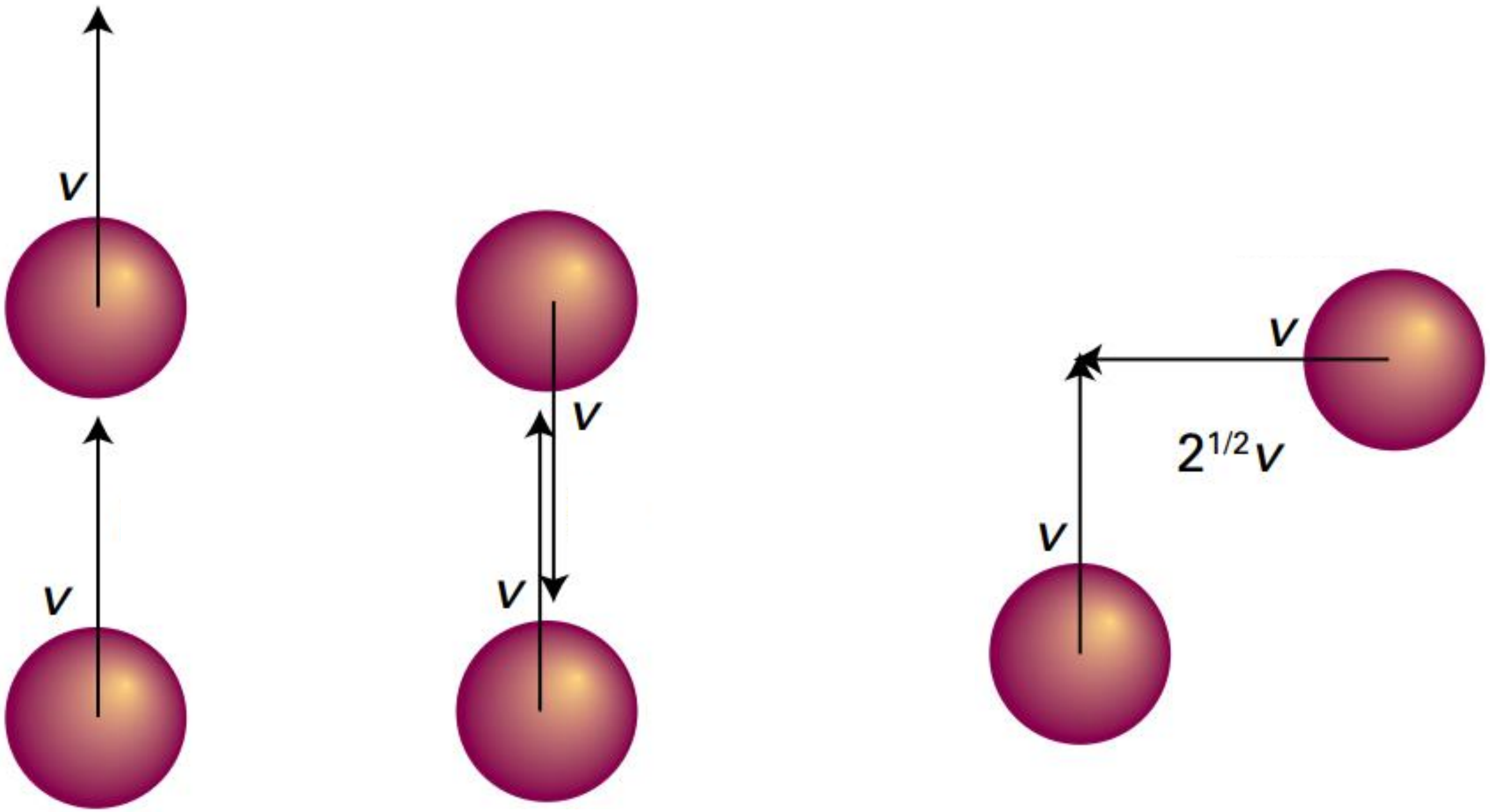


Relative speed of a molecule w.r.t. another

velocities are equally likely to point in any direction



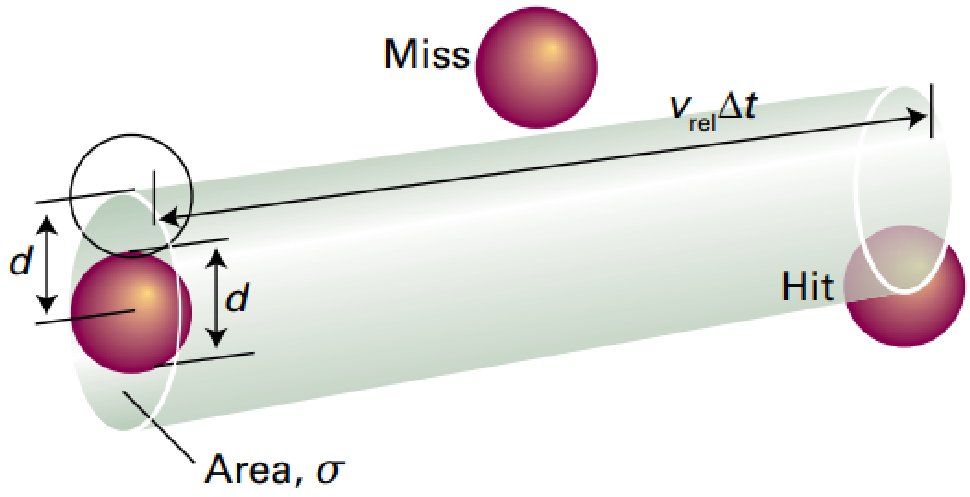
Relative speed of a molecule w.r.t. another



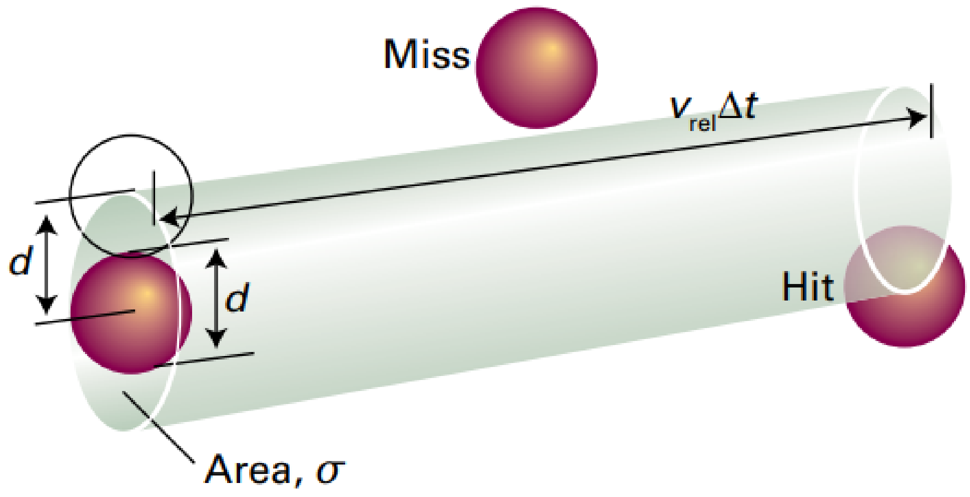
mean relative speed, $v_{\text{rel}} = 2^{1/2} v_{\text{mean}}$

Collision frequency

Collision frequency

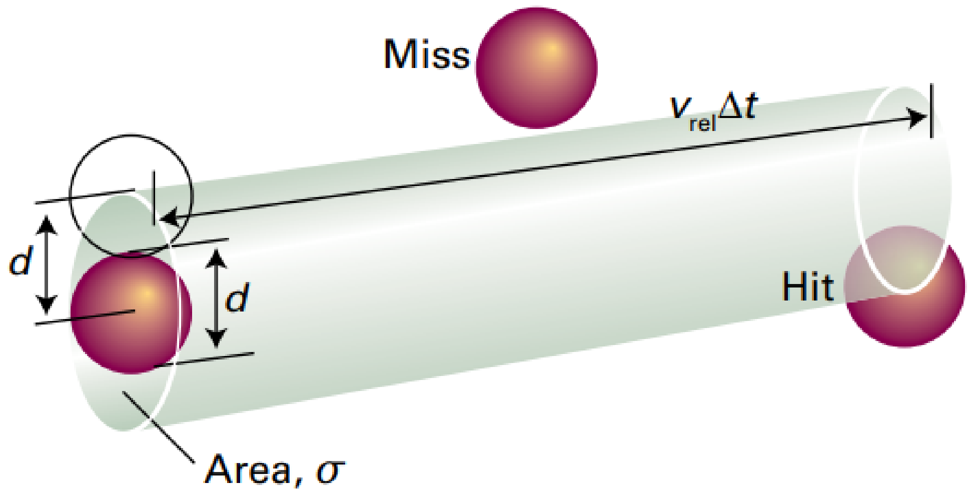


Collision frequency



number of stationary molecules $\mathcal{N}\sigma v_{rel}\Delta t$, number density $\mathcal{N}=N/V$;

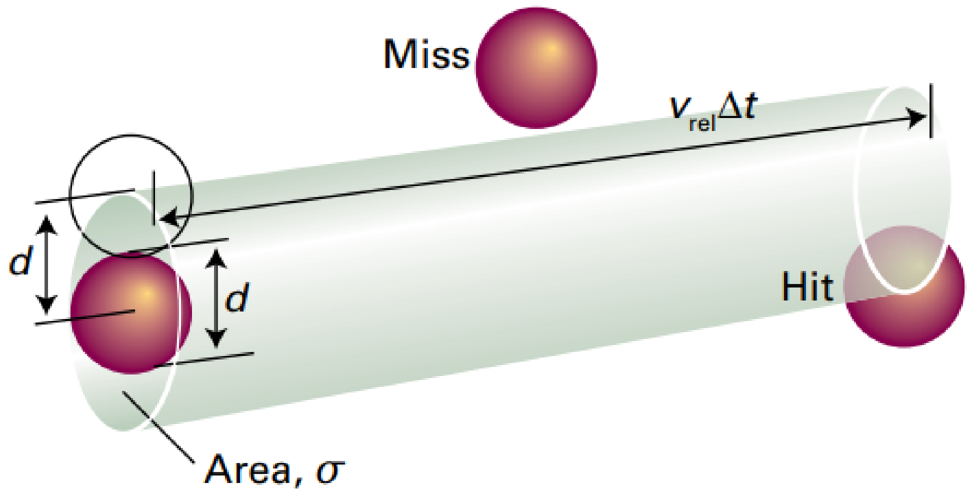
Collision frequency



number of stationary molecules $\mathcal{N}\sigma v_{rel}\Delta t$

The collision frequency z $z = \sigma v_{rel}\mathcal{N}$

Collision frequency



number of stationary molecules $\mathcal{N}\sigma v_{rel}\Delta t$

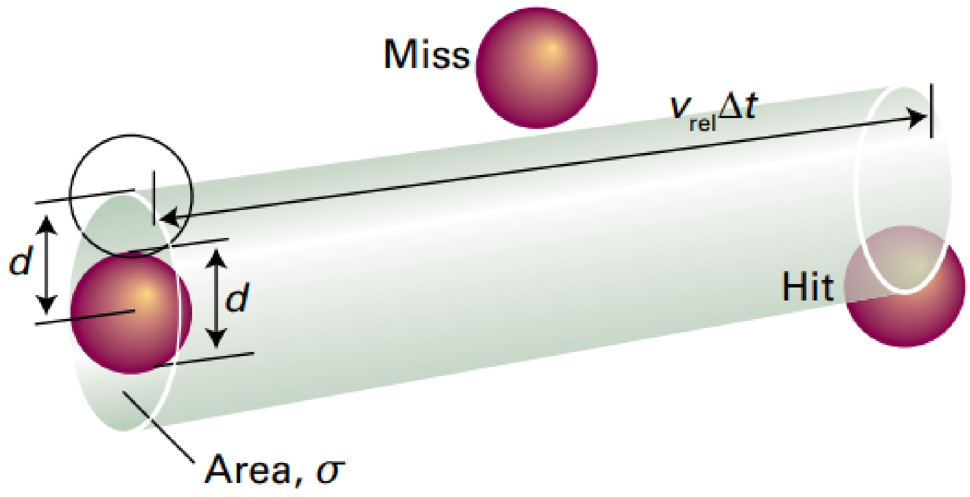
The collision frequency z $z = \sigma v_{rel}\mathcal{N}$

collision cross-section

	σ/nm^2
C_6H_6	0.88
CO_2	0.52
He	0.21
N_2	0.43

* More values are given in the *Resource section*.

Collision frequency



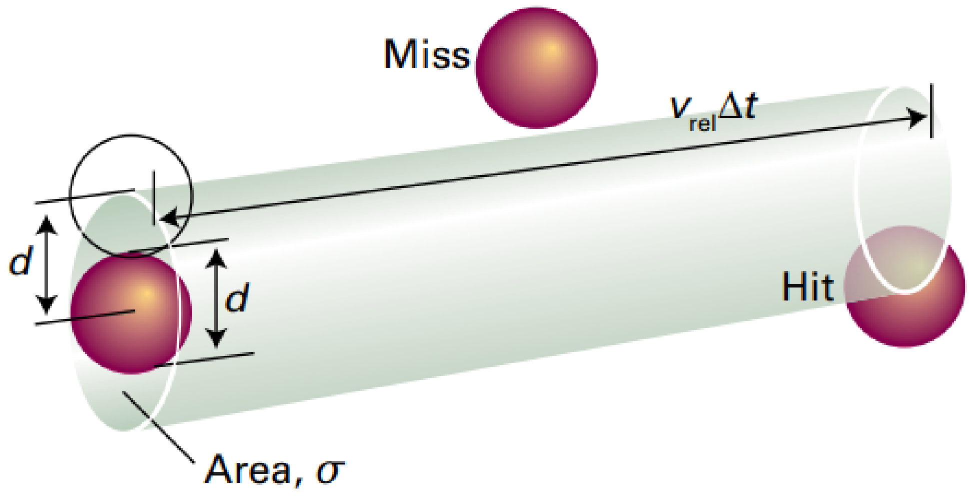
number of stationary molecules $\mathcal{N}\sigma v_{rel}\Delta t$,

number density $\mathcal{N}=N/V$;

The collision frequency z $z=\sigma v_{rel}\mathcal{N}$

$$\mathcal{N}=\frac{N}{V}=\frac{nN_A}{V}=\frac{nN_A}{nRT/p}=\frac{pN_A}{RT}=\frac{p}{kT}$$

Collision frequency



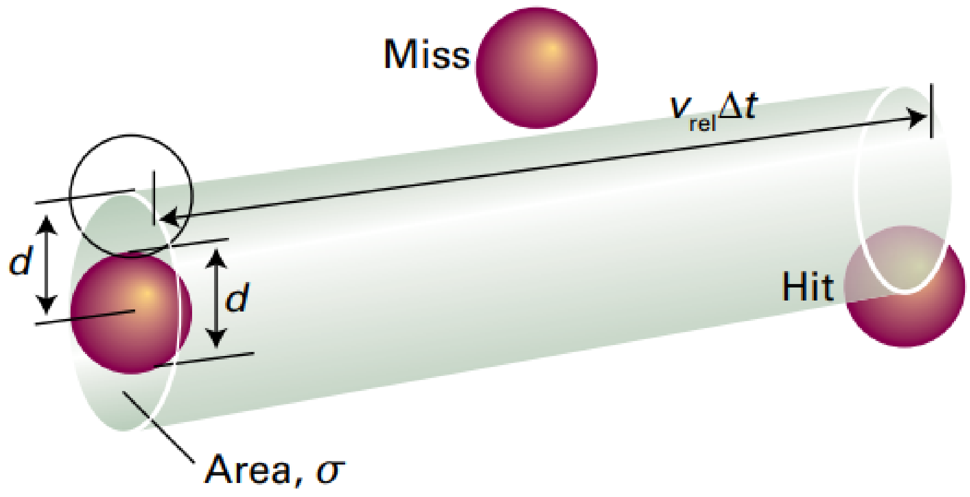
number of stationary molecules $\mathcal{N}\sigma v_{rel}\Delta t$, number density $\mathcal{N} = N/V$;

The collision frequency z $z = \sigma v_{rel}\mathcal{N}$

$$\mathcal{N} = \frac{N}{V} = \frac{nN_A}{V} = \frac{nN_A}{nRT/p} = \frac{pN_A}{RT} = \frac{p}{kT}$$

$$\boxed{z = \frac{\sigma v_{rel} p}{kT}}$$

Collision frequency



	σ/nm²
C_6H_6	0.88
CO_2	0.52
He	0.21
N_2	0.43

* More values are given in the *Resource section*.

$$z = \frac{(0.45\times10^{-18}\,\mathrm{m}^2)\times(671\,\mathrm{m\,s^{-1}})\times(1.01\times10^5\,\mathrm{Pa})}{(1.381\times10^{-23}\,\mathrm{J\,K^{-1}})\times(298\,\mathrm{K})}$$

$$= 7.4\times10^9\,\mathrm{s^{-1}}$$

number of stationary molecules $\mathcal{N}\sigma v_{rel}\Delta t$

The collision frequency z $z = \sigma v_{rel}\mathcal{N}$

$$\boxed{z = \frac{\sigma v_{rel} p}{kT}}$$

Mean free path

Mean free path

$$\lambda = \frac{v_{\text{rel}}}{z}$$

Mean free path

$$\lambda = \frac{v_{\text{rel}}}{z} \xrightarrow{z = \frac{\sigma v_{\text{rel}} p}{kT}} \lambda = \frac{kT}{\sigma p}$$

Mean free path

$$\lambda = \frac{v_{\text{rel}}}{z} \xrightarrow{z = \frac{\sigma v_{\text{rel}} p}{kT}} \lambda = \frac{kT}{\sigma p}$$

v_{rel} = 671ms^{-1} (for N_2 molecules at 25 °C)

$$z = 7.4\times10^9\ \text{s}^{-1}$$

$$\lambda = \frac{671\,\text{m}\,\text{s}^{-1}}{7.4\times10^9\ \text{s}^{-1}} = 9.1\times10^{-8}\,\text{m}$$