2. Properties of Gases

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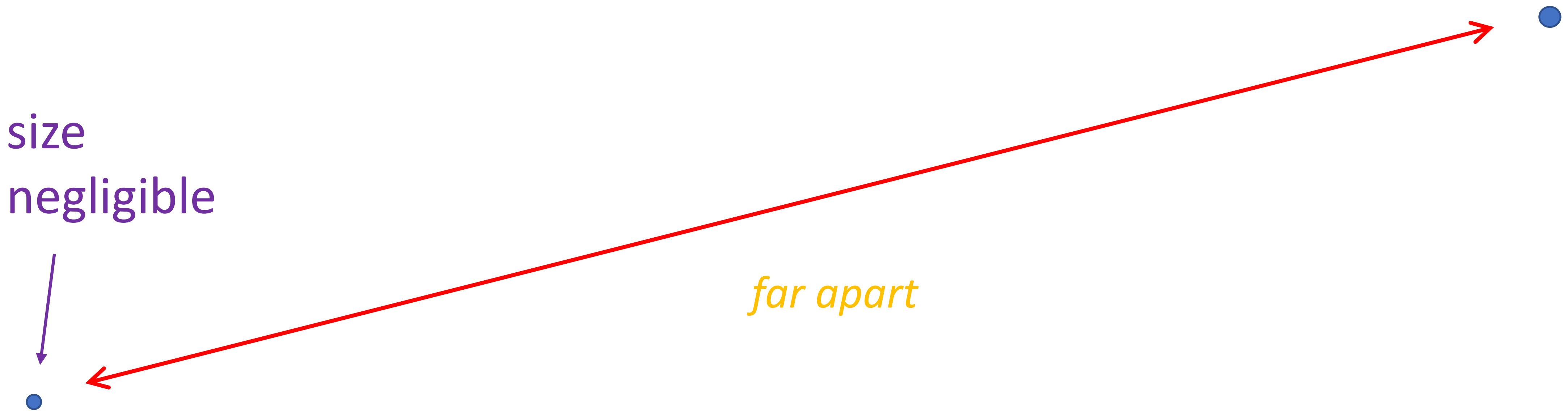
Gas **vs.** **Liquid/ Solid**

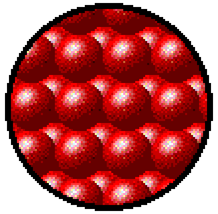
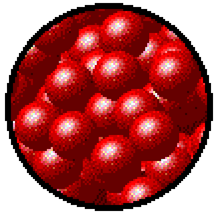
Kinetic Molecular Theory (KMT)

Describes the ideal behavior of gases:

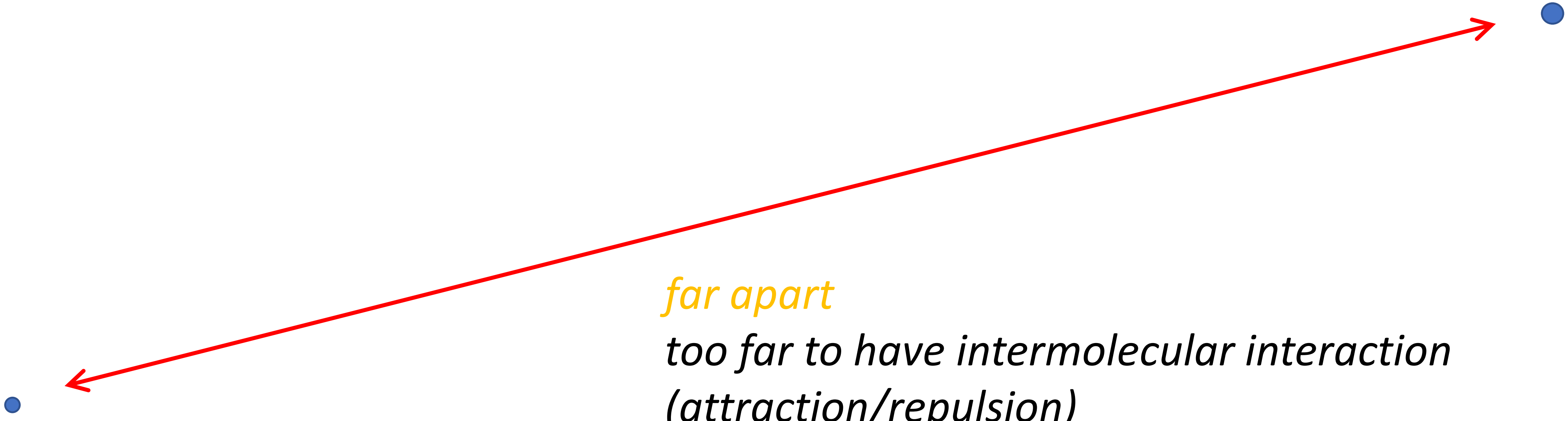
1) The volume of the molecule is negligible compared to the large distances between the molecules.
2) Gas molecules are so far apart, that they do NOT have intermolecular interaction.
3) Gas molecules do NOT interact, but they move around fast and they constantly collide with one another.
4) Kinetic Energy:
    1. Same temperature, same average kinetic energy (KE_{avg}).
    2. The higher the temperature, the higher the kinetic energy (KE_{avg}).

KMT1 The volume of the molecule is negligible compared to the large distances between the molecules.



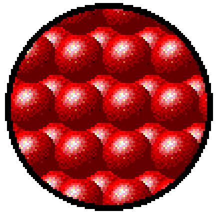
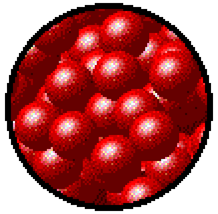
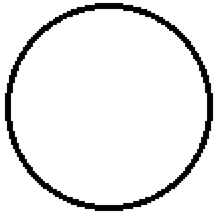
	Solid	Liquid	Gas
Microscopic			

KMT2 Gas molecules are so far apart, that they do NOT have intermolecular interaction.



far apart

too far to have intermolecular interaction (attraction/repulsion)

	Solid	Liquid	Gas
Microscopic			

Ideal Gas/Ideal Gas Law/Ideal Gas Equation

- **Ideal Gas**: behaves in accordance to combined gas law, follows postulates of KMT
- Combined Gas Law: $$\frac{PV}{nT} = constant = \boldsymbol{R}$$ T should be in Kelvins (K)!!
- This rearranges to: $\boldsymbol{PV = nRT}$ **Ideal Gas Equation**

- **R = universal gas constant**
- Units and Values of R: $$\boldsymbol{R = 0.08206\,\frac{L \cdot atm}{mol \cdot K}}$$

Chose the appropriate R value according to the units of the variables you use.

SI unit: $$\boldsymbol{R = 8.3145\,\frac{m^3 Pa}{mol \cdot K} = 8.3145\,\frac{L \cdot kPa}{mol \cdot K} = 8.3145\,JK^{-1}mol^{-1}}$$

Ideal vs. Real Gases

- KMT1 and KMT2 are assumptions for the ideal gas equation.
  1) The volume of the molecule is negligible compared to the large distances between the molecules.
  2) Gas molecules are so far apart, that they do NOT have intermolecular interaction.

- These assumptions are valid at STP, but not at higher pressures:
  1) Volume occupied by gas molecules is not negligible.
  2) Attractive forces between gas molecules are significant.

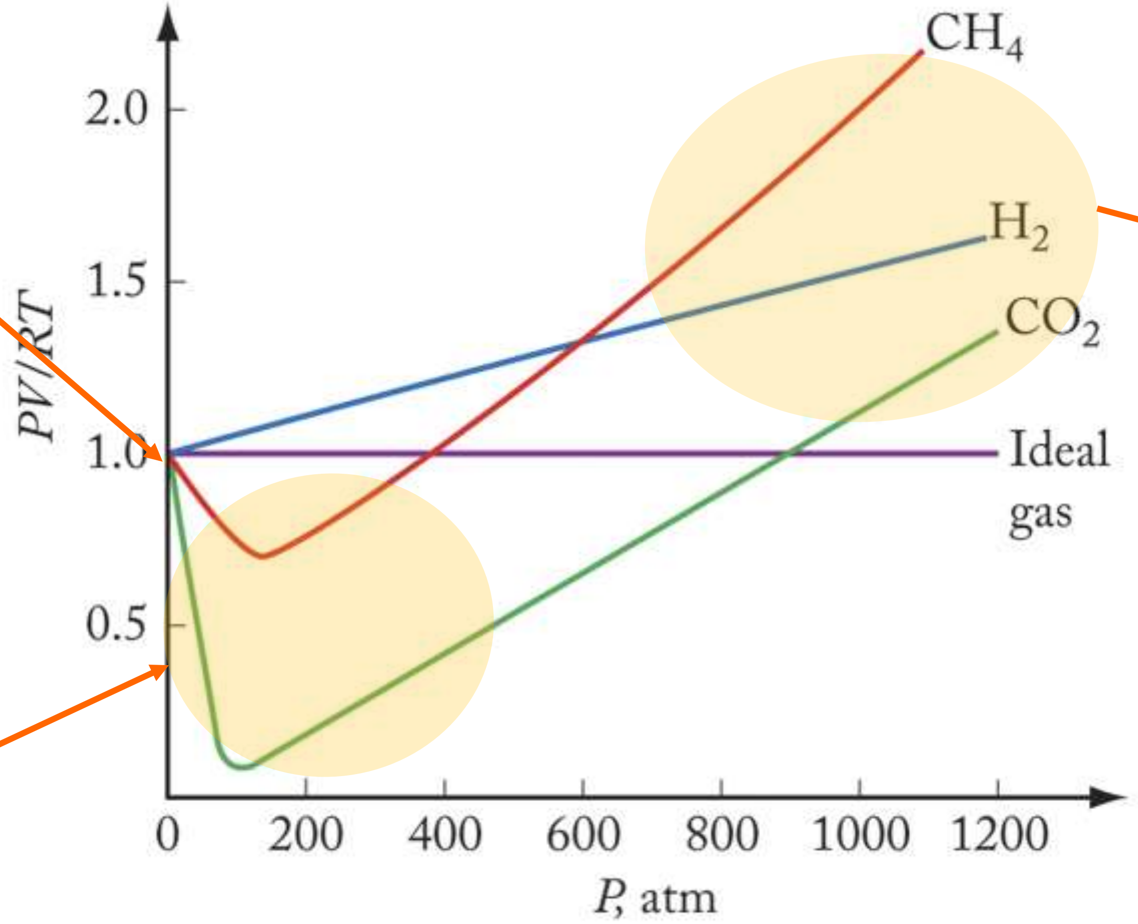
Deviations from the Ideal Behavior

- For ideal gas, PV = nRT, PV/nRT = 1
- Define compressibility factor $Z \equiv \frac{PV}{nRT}$
- Z≠1 for real gases, especially for higher P and lower V.

Deviations from the Ideal Behavior

P → 0
⇒ V increase
⇒ distance between molecules increase
⇒ ideal behavior
⇒ Z → 1

attractive forces (longer range force)
⇒ PV/nRT < 1



volume of gases become significant
⇒ repulsive force (shorter range force)
⇒ PV/nRT > 1

P increase
⇒ V decrease
⇒ distance between molecules decrease

distance between molecules increase

distance between molecules decrease

van der Waals equation

- Corrections to the ideal gas equation

volume without the gas

$$\left[P + a\left(\frac{n}{V}\right)^2\right][V - nb] = nRT$$

measured pressure

pressure if there were no intermolecular force

corrects for intermolecular interaction

depends on square of the concentration (n/V) : interaction of two particles

corrects for volume taken up by gas

London dispersion, dipole-dipole, hydrogen bonding, dipole-induced dipole interactions
$\Rightarrow$ contributes to 'a' value
$\Rightarrow$ van der Waals forces

a, b: van der Waals constants (experimental)

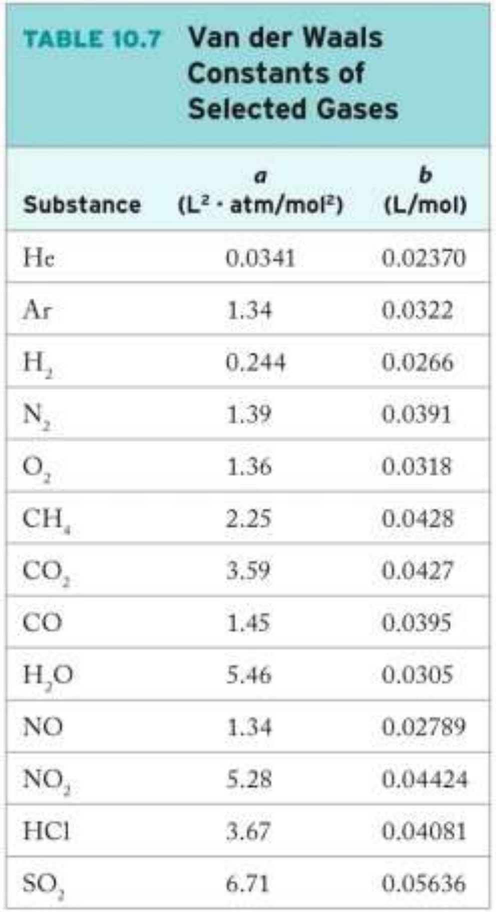
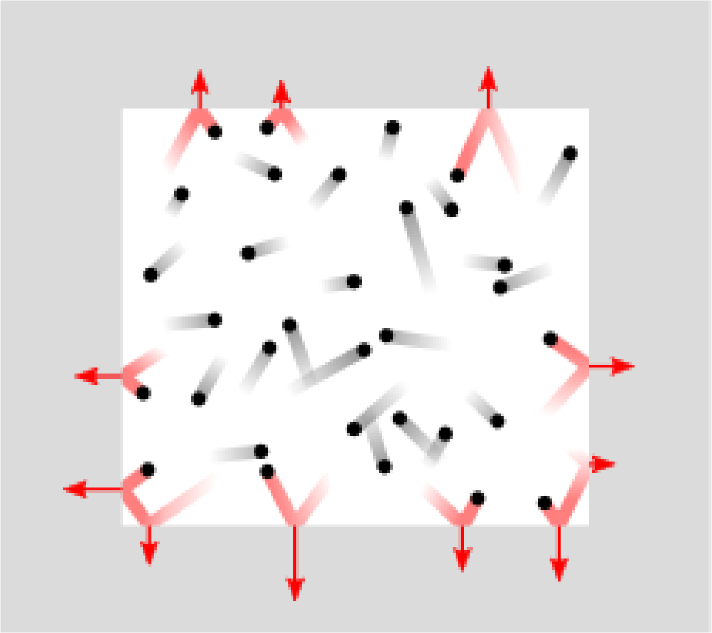


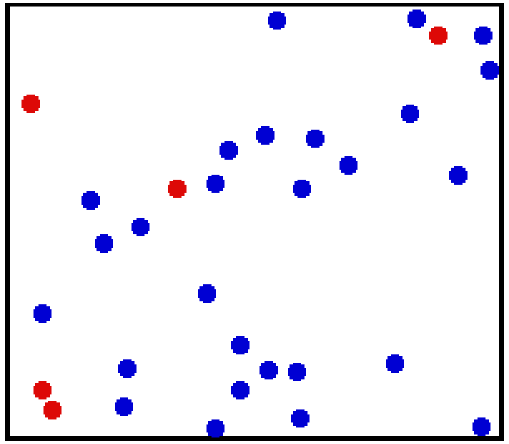
TABLE 10.7 **Van der Waals Constants of Selected Gases**

Substance	*a* ($L^2 \cdot atm/mol^2$)	*b* (L/mol)
He	0.0341	0.02370
Ar	1.34	0.0322
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CO	1.45	0.0395
H_2O	5.46	0.0305
NO	1.34	0.02789
NO_2	5.28	0.04424
HCl	3.67	0.04081
SO_2	6.71	0.05636

In Molecular Level,

- Gas molecules are constantly moving around, and the pressure of the gas is exerted by the force of the gas constantly colliding on the wall of the surface.





Pressure Units

- Unit pressure in SI Units: **Pa (pascal)**

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} \qquad 1\ \text{Pa} = \frac{1\ \text{N}}{1\ \text{m}^2}$$

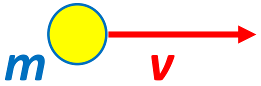
- 1 atm = 101,325 Pa = 101.325 kPa = 760 mmHg = 760 Torr
- 1 bar = 100,000 Pa = 100 kPa
- 1 atm = 1.01325 bar
- 1 atm = 14.7 psi (pounds per square inch)

Pressure Unit Conversion

- 1021 millibar in Pa?
- 1021 millibar in atm?
- 100 Torr in Pa?
- 100 Torr in atm?
- 30 psi in atm?
- 30 psi in Pa?

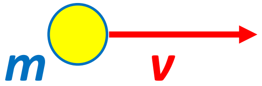
KMT4: KE_{avg} vs. T

- Kinetic Energy (translational) of a ball of mass m and velocity v:



$$KE = \frac{1}{2}mv^2$$

- Kinetic Energy (translational) of a gas molecule of mass m and velocity v:



$$KE = \frac{1}{2}mv^2$$

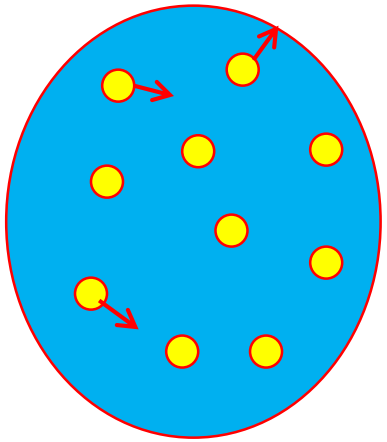
KMT4: KE_{avg} vs. T

- How does the average kinetic energy of a gas molecule change with temperature T ?

The average KE increases linearly with T

at T, $\textbf{average } \boldsymbol{KE} = \frac{\mathbf{3}}{\mathbf{2}}\boldsymbol{k_B T}$

- k_B : Boltzmann constant = 1.381×10^{-23} J K^{-1}
- (gas constant for ONE molecule $k_B = \frac{R}{N_A}$, N_A : Avogadro’s number)

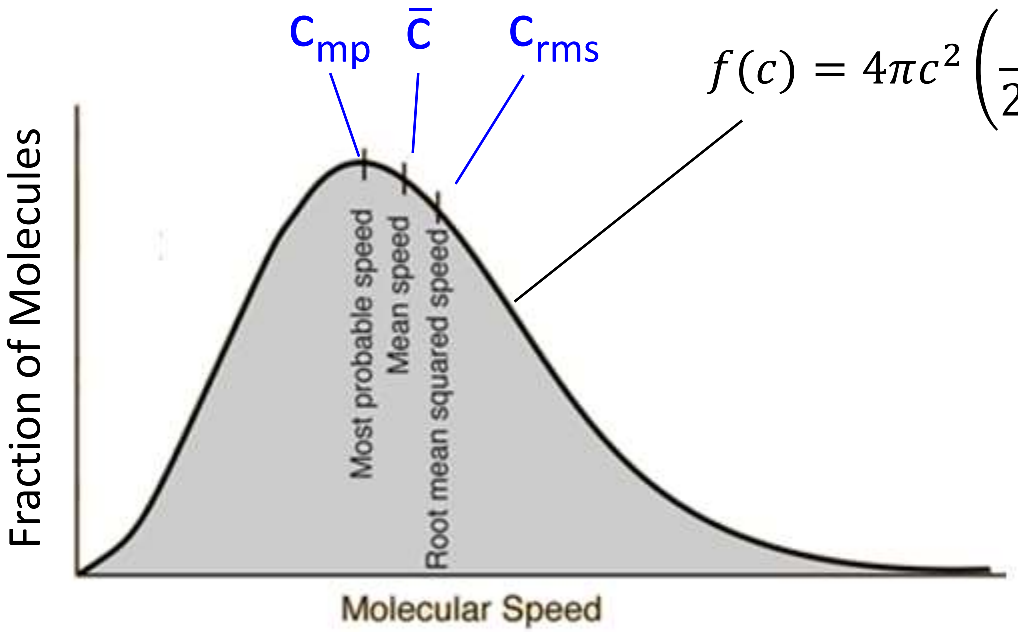


- Average KE of 1 mol of gas?

$$\textbf{average } \boldsymbol{KE} = \frac{\mathbf{3}}{\mathbf{2}}\boldsymbol{k_B T} \times \boldsymbol{N_A} = \frac{\mathbf{3}}{\mathbf{2}}\boldsymbol{RT}$$

KMT4: KE_{avg} vs. T

- At a certain temperature, there is a distribution in the speed and kinetic energy of gases.
- The average of the kinetic energy is **average $KE = \frac{3}{2} k_B T$.**



$$f(c) = 4\pi c^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mc^2}{2k_B T}} dc$$

- c_{mp} : most probable speed
- $\bar{c}$: average speed

$$\bar{c} = \frac{c_1 + c_2 + \cdots + c_n}{n}$$

- c_{rms} : root-mean-square speed

$$c_{rms} = \sqrt{\frac{{c_1}^2 + {c_2}^2 + \cdots + {c_n}^2}{n}}$$

useful for KE calculation ($1/2mv^2$)

KMT4: KE_{avg} vs. T

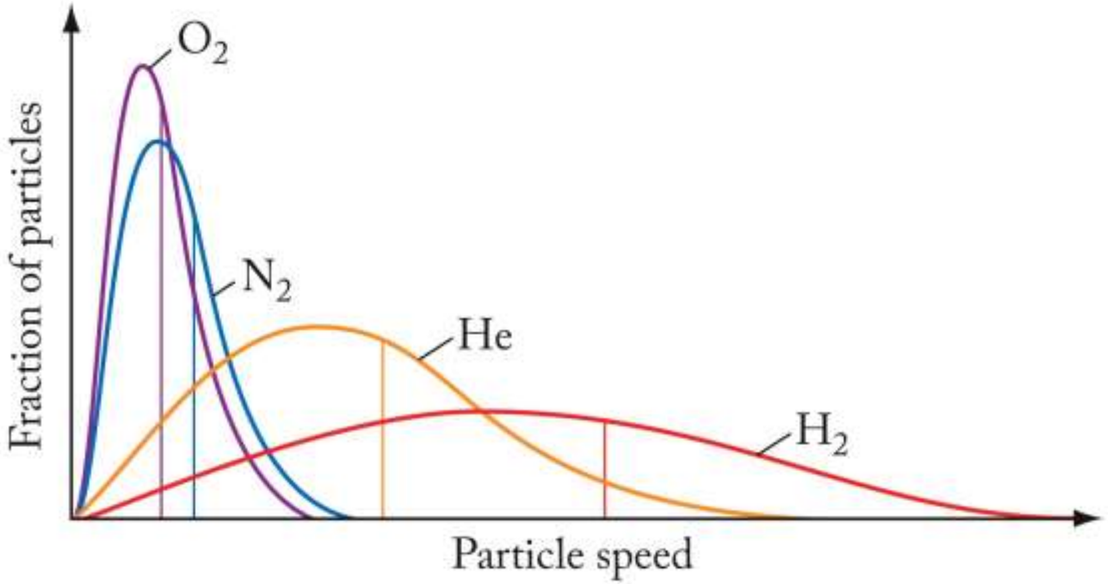
- $KE_{avg} = \frac{\frac{1}{2}m{c_1}^2 + \frac{1}{2}m{c_2}^2 + \cdots + \frac{1}{2}m{c_n}^2}{n} = \frac{1}{2}m\frac{{c_1}^2 + {c_2}^2 + \cdots + {c_n}^2}{n} = \frac{1}{2}m{c_{rms}}^2$

- $KE_{avg} = \frac{1}{2}m{c_{rms}}^2 = \frac{3}{2}k_B T$ rearrange

- $c_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$ $M = mN_A$ $R = k_B N_A$

- $c_{mp} = \sqrt{\frac{2RT}{M}}$ $\bar{c} = \sqrt{\frac{8RT}{\pi M}}$ => speed of gas molecules $\propto \sqrt{\frac{1}{M}}$

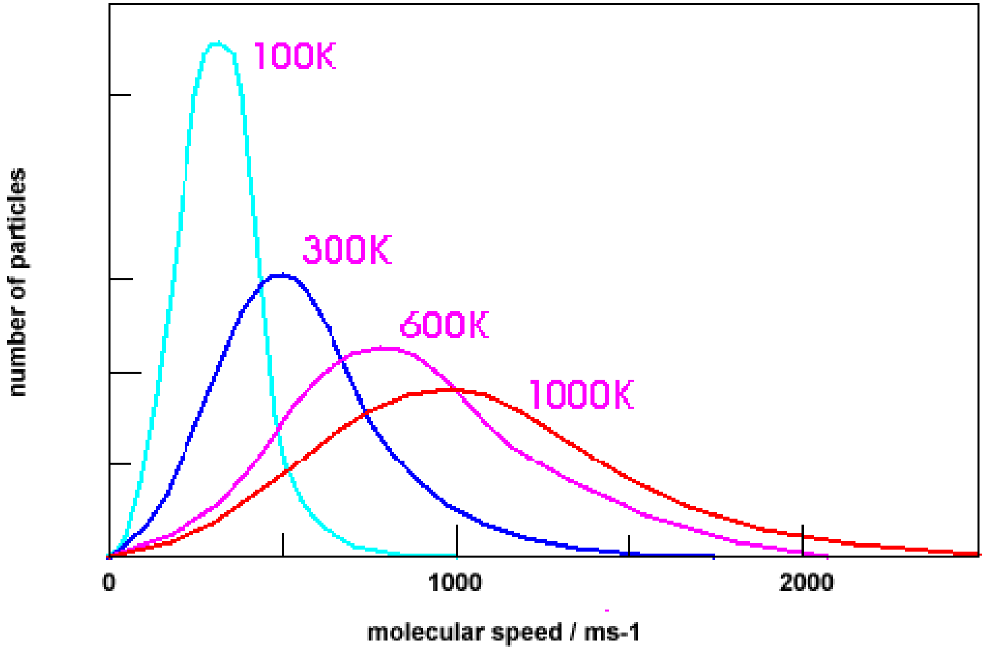
KMT4: KE_{avg} vs. T



- speed of gas molecules $\propto \sqrt{\frac{1}{M}}$
- $\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$
- The heavier the gas, slower the speed.
- Different molecules have the same kinetic energy at the same temperature, but they have different speed.
- $KE = \frac{1}{2} m_1 {v_1}^2 = \frac{1}{2} m_2 {v_2}^2$
- $\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$

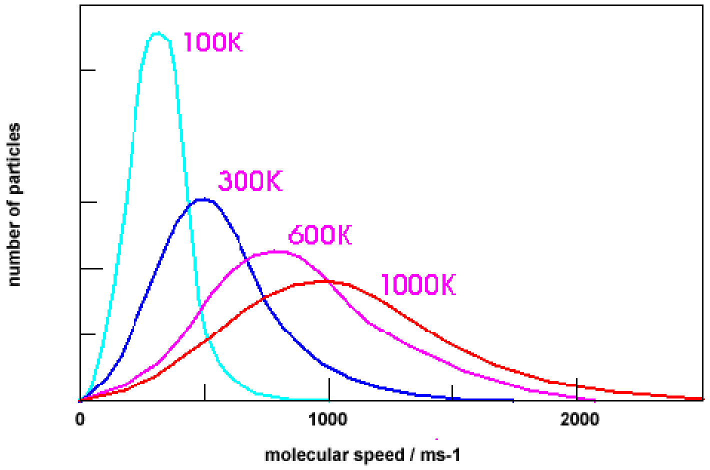
KMT4: KE_{avg} vs. T

- For the same molecule, **average** $\boldsymbol{KE = \frac{3}{2} k_B T}$
- Kinetic energy ($1/2mv^2$) increases with temperature. Therefore, molecule speed also increases with temperature.

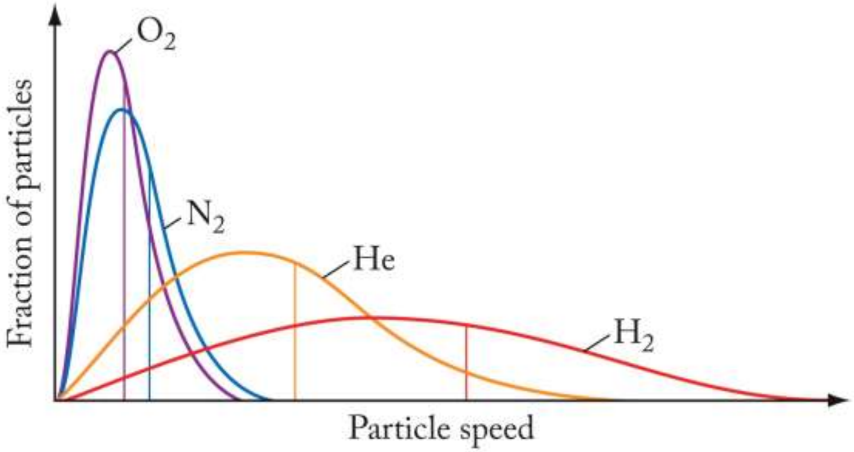


KMT4: KE_{avg} vs. T

- **higher T, higher speed**



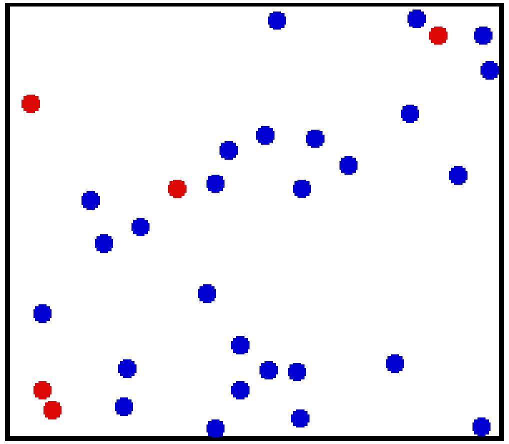
- **heavier molecule, lower speed**

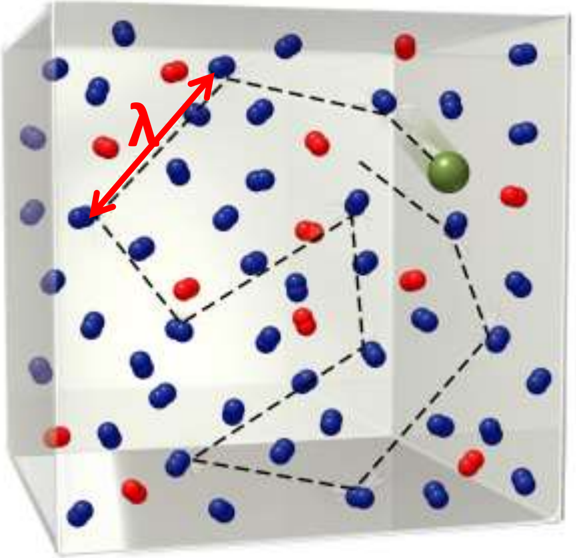


- Calculate the values of c_{mp}, $\bar{c}$, and c_{rms} for O_2 at 300 K.

KMT3

Gas molecules do NOT interact, but they move around fast and they **constantly collide** with one another.



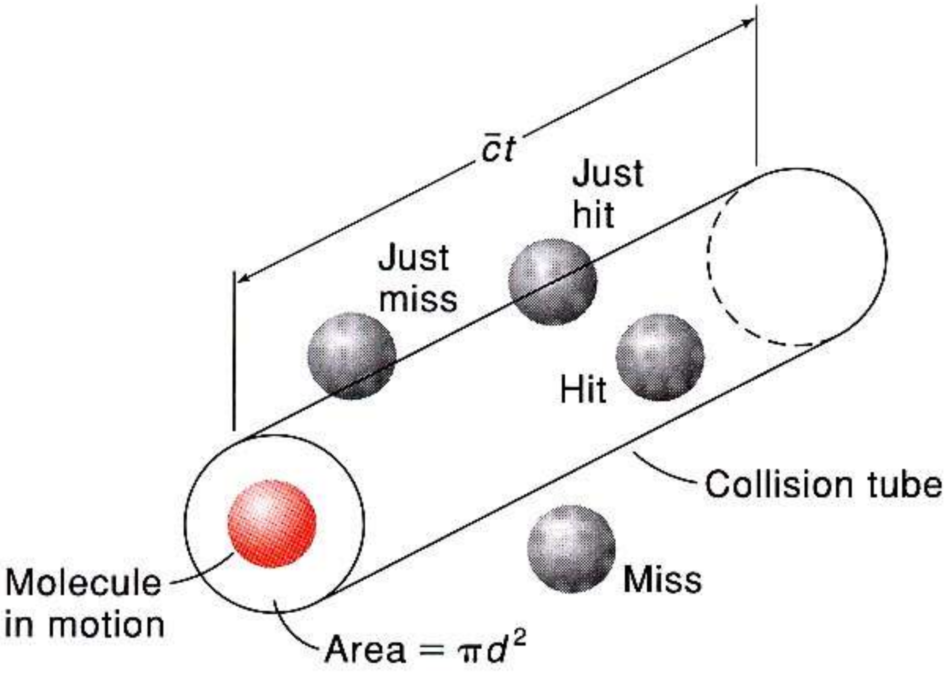


- **Mean-free-path (λ)**:
- average distance traveled by a molecule between successive collisions
- ~ 640 Å (= $6.4\text{x}10^{-8}$ m) at STP

- **Collision frequency (Z_1)**:
- collision per second for one molecule
- $7.5\text{x}10^{9}$ collisions s^{-1} at STP

KMT3 Gas molecules **constantly collide** with one another.

- Calculating the mean-free-path and collision frequency



- In a given instant, during time t,
- A molecule moves $\bar{c}$ t (distance = speed x time).
- It sweeps out a collision tube with a cross-sectional area πd^2.
- There are N molecules per unit volume.

How many molecules have the center in the cylinder?

= volume of the cylinder x $\left(\frac{N}{V}\right)$

= $\pi d^2 \, \bar{c} \, t$ x $\left(\frac{N}{V}\right)$

= # of collision of one molecule *in time t*

KMT3 Gas molecules **constantly collide** with one another.

of collision of one molecule per unit time = $\pi d^2 \bar{c} \times \left(\frac{N}{V}\right)$

When other molecules are moving, use relative speed $\sqrt{2}\bar{c}$ instead of $\bar{c}$.

# of collision of one molecule per unit time

= Collision Frequency $Z_1 = \sqrt{2}\, \pi d^2 \bar{c} \times \left(\frac{N}{V}\right)$

KMT3 Gas molecules **constantly collide** with one another.

of collision of one molecule per unit time

= Collision Frequency $Z_1 = \sqrt{2}\,\pi d^2\,\bar{c} \times \left(\frac{N}{V}\right)$

# of collision for N molecules per unit volume per unit time

= Total number of binary collisions Z_{11}

$= \frac{1}{2} Z_1 \left(\frac{N}{V}\right) = \frac{\sqrt{2}}{2}\pi d^2\,\bar{c} \times \left(\frac{N}{V}\right)^2$

not to count same
collision twice

KMT3 Gas molecules **constantly collide** with one another.

Collision Frequency Z_1 :
# of collision of one molecule per second

$\frac{1}{Z_1}$: second per collision of one molecule

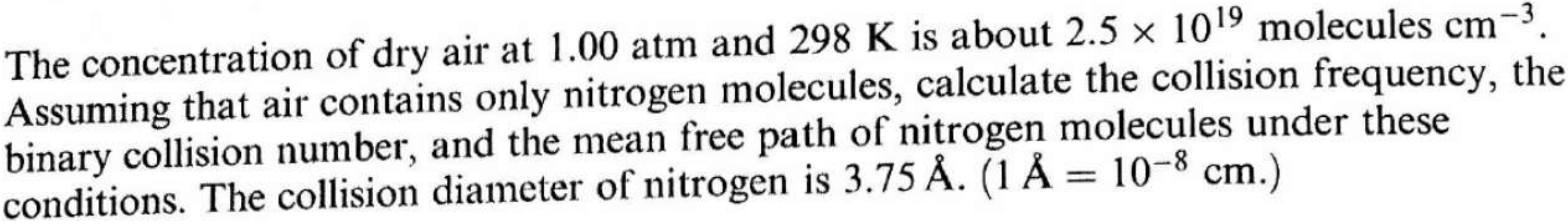
Mean-free-path (λ): average *distance* traveled by a molecule between successive collisions

λ = average speed x average time between collisions

$$= \bar{c} \times \frac{1}{Z_1} = \bar{c} \times \frac{1}{\sqrt{2}\,\pi d^2\, \bar{c} \times \left(\frac{N}{V}\right)} = \frac{1}{\sqrt{2}\,\pi d^2 \times \left(\frac{N}{V}\right)}$$

mean free path $\lambda = \frac{k_B T}{\sqrt{2}\,\pi d^2\, p}$

The concentration of dry air at 1.00 atm and 298 K is about 2.5×10^{19} molecules cm^{-3}. Assuming that air contains only nitrogen molecules, calculate the collision frequency, the binary collision number, and the mean free path of nitrogen molecules under these conditions. The collision diameter of nitrogen is 3.75 Å. (1 Å = 10^{-8} cm.)



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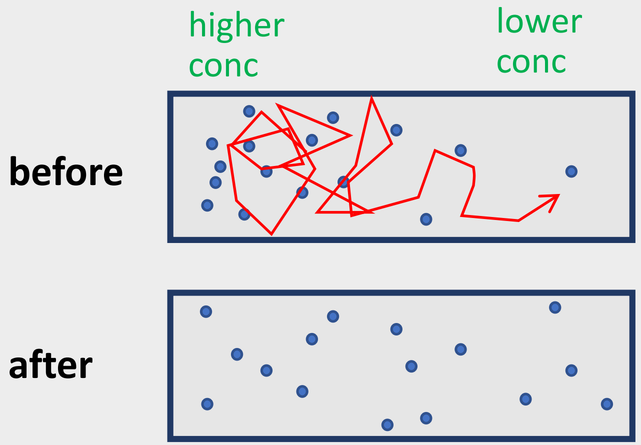
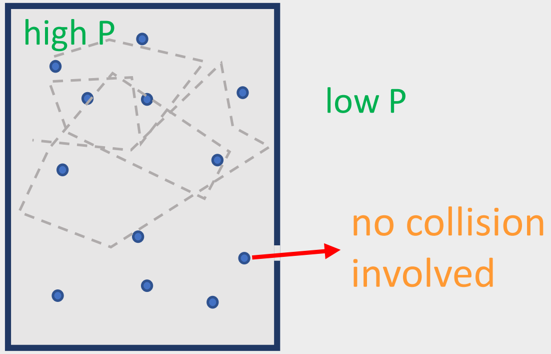
Diffusion

- *Net* movement of molecules from high to low concentration.
- Involves multiple collisions.
- Bulk flow. Slow process.
- 640 Å, ~10^{10} collisions per second
- Odor spreading through air is slow because the molecules have to collide their way through.

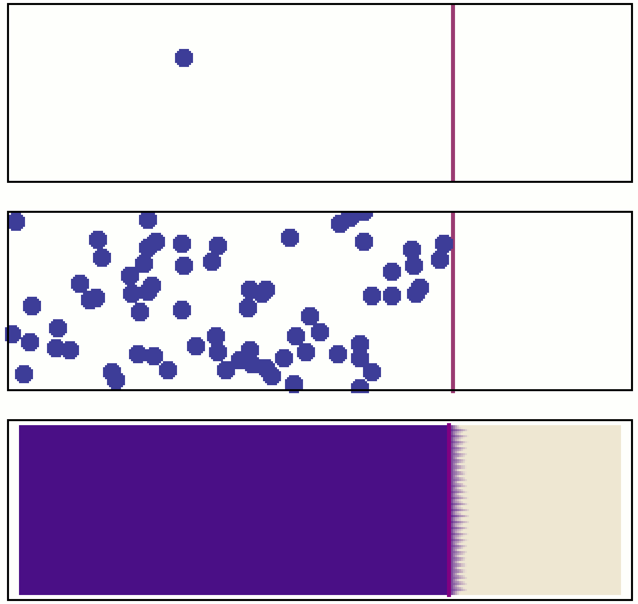


Effusion

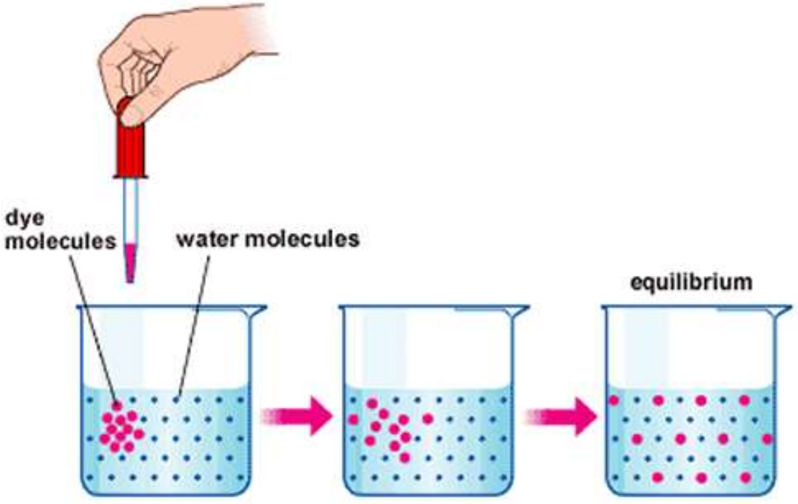
- Movement of a gas molecule one molecule at a time.
- Does NOT involve collision with other molecules.
- Movement of gas through a small pinhole
- λ > diameter of pinhole
- Escape of gas through balloon wall



Diffusion



Diffusion in Liquid Phase

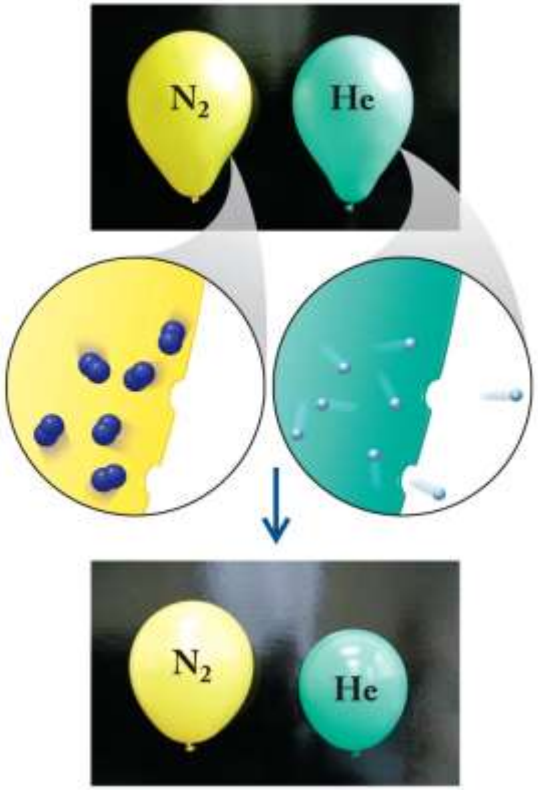


Diffusion

Diffusion and Effusion

- For both diffusion and effusion,
- diffusion/effusion speed $\propto \sqrt{\frac{1}{M}}$
- $\frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$

- Graham’s Law of Effusion



the volume of the
helium balloon
decreases much faster

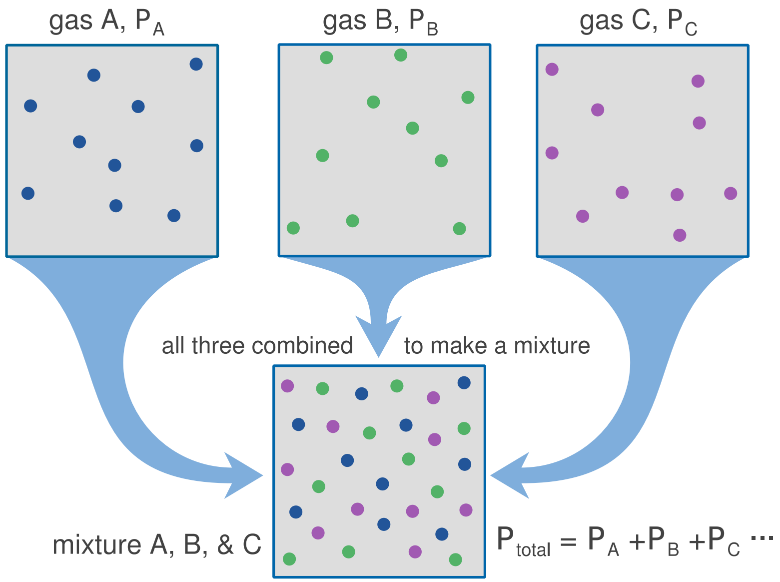
Dalton’s law of partial pressures

When n types of different gases are mixed,

$$P_{total} = P_1 + P_2 + \dots + P_n$$

P_n : partial pressure of the gas

The total pressure is the sum of all partial pressures



Mole Fraction and Partial Pressure

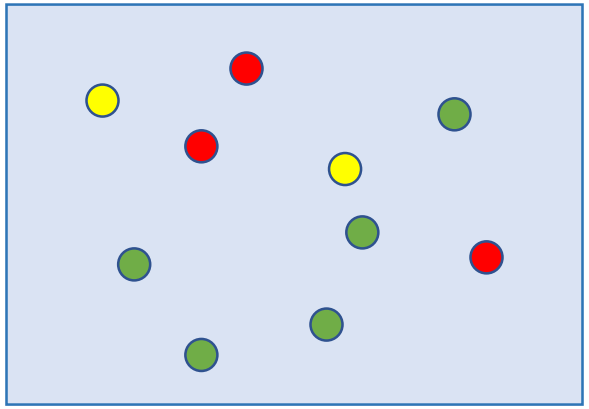
- **Mole Fraction**
  - Ratio of the # of moles of a given component to the total # of moles in a mixture

$$x_1 = \frac{n_1}{n_{\text{total}}} = \frac{n_1}{n_1 + n_2 + n_3 + \ldots}$$

- n ∝ P, therefore,

$$\chi_1 = \frac{n_1}{n_{total}} = \frac{P_1}{P_{total}}$$

$$P_1 = \chi_1 P_{total}$$



N_2	O_2	H_2	Total
2 mol	3 mol	5 mol	10 mol

Then, partial pressures,

$$P_{N2} : P_{O2} : P_{H2}$$

$$= 2 : 3 : 5$$

Pressure is directly proportional to the number of molecules no matter what the gas is! (for ideal gases)

Mole Fractions

$$\chi_{N2} = \frac{2\,mol}{10\,mol} = 0.2$$

$$\chi_{O2} = \frac{3\,mol}{10\,mol} = 0.3$$

$$\chi_{H2} = \frac{5\,mol}{10\,mol} = 0.5$$

Partial Pressures

$$P_{N2} = 0.2 \times P_{total}$$

$$P_{O2} = 0.3 \times P_{total}$$

$$P_{H2} = 0.5 \times P_{total}$$

$n_{total} = 7\,mol + 2\,mol + 1\,mol = 10\,mol$

A gas mixture contains 7 mol N_2, 2 mol H_2, and 1 mol CH_4. What is the mole fraction of N_2 in the mixture? Calculate the partial pressure of N_2 if the total pressure of the mixture is 48 atm.

$$\chi_{N_2} = \frac{n_{N_2}}{n_{total}} = \frac{7\,mol}{10\,mol} = 0.7$$

$$P_{N_2} = \chi_{N_2} P_{total} = 0.7 \times 48\,atm = 33.6\,atm$$