States of Matter
Lesson 4.6

CHEMISTRY 2
HONORS

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Molecular Effusion and Diffusion

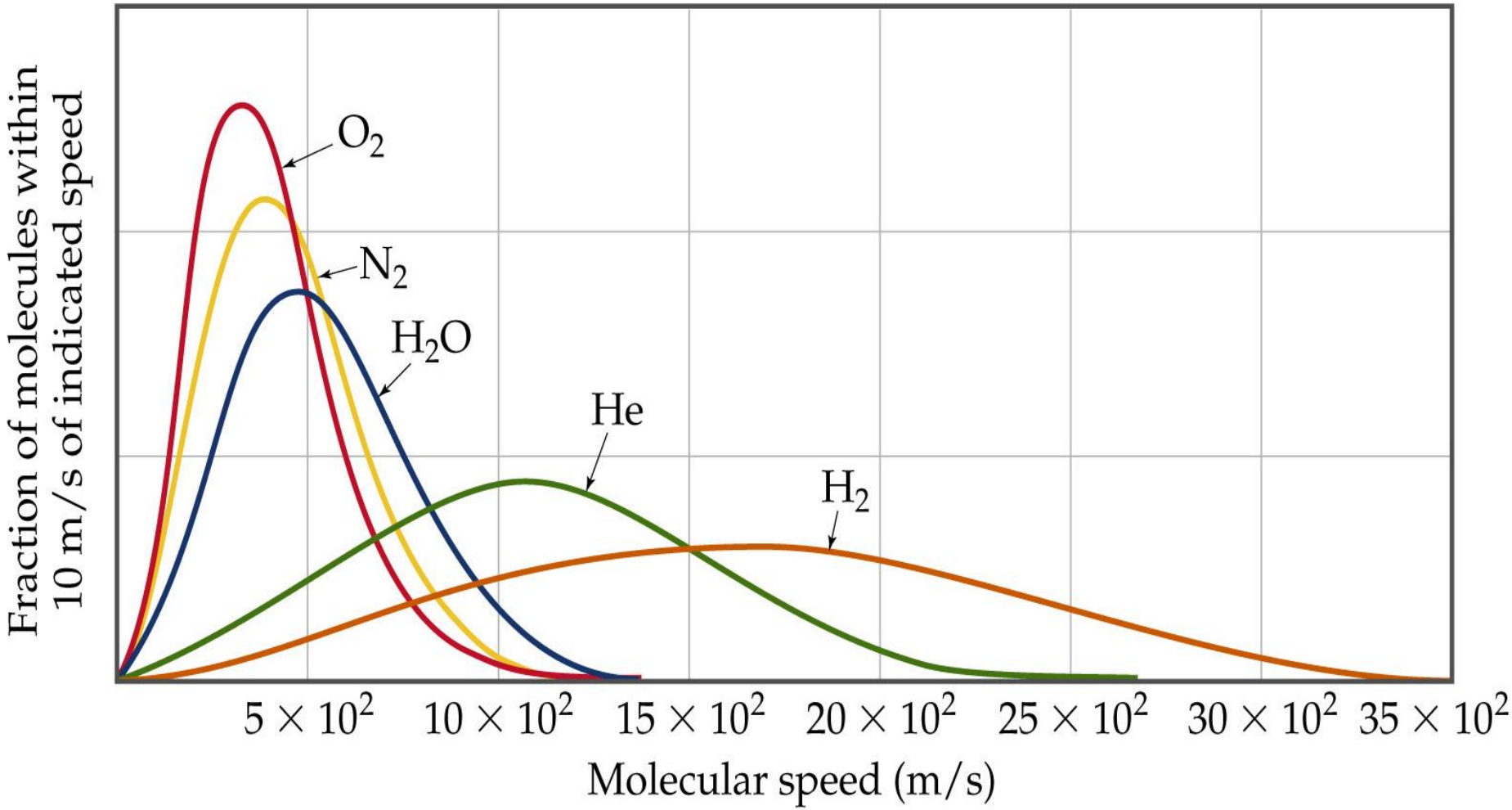
- As kinetic energy increases, the velocity of the gas molecules increases.
- Average kinetic energy of a gas is related to its mass:

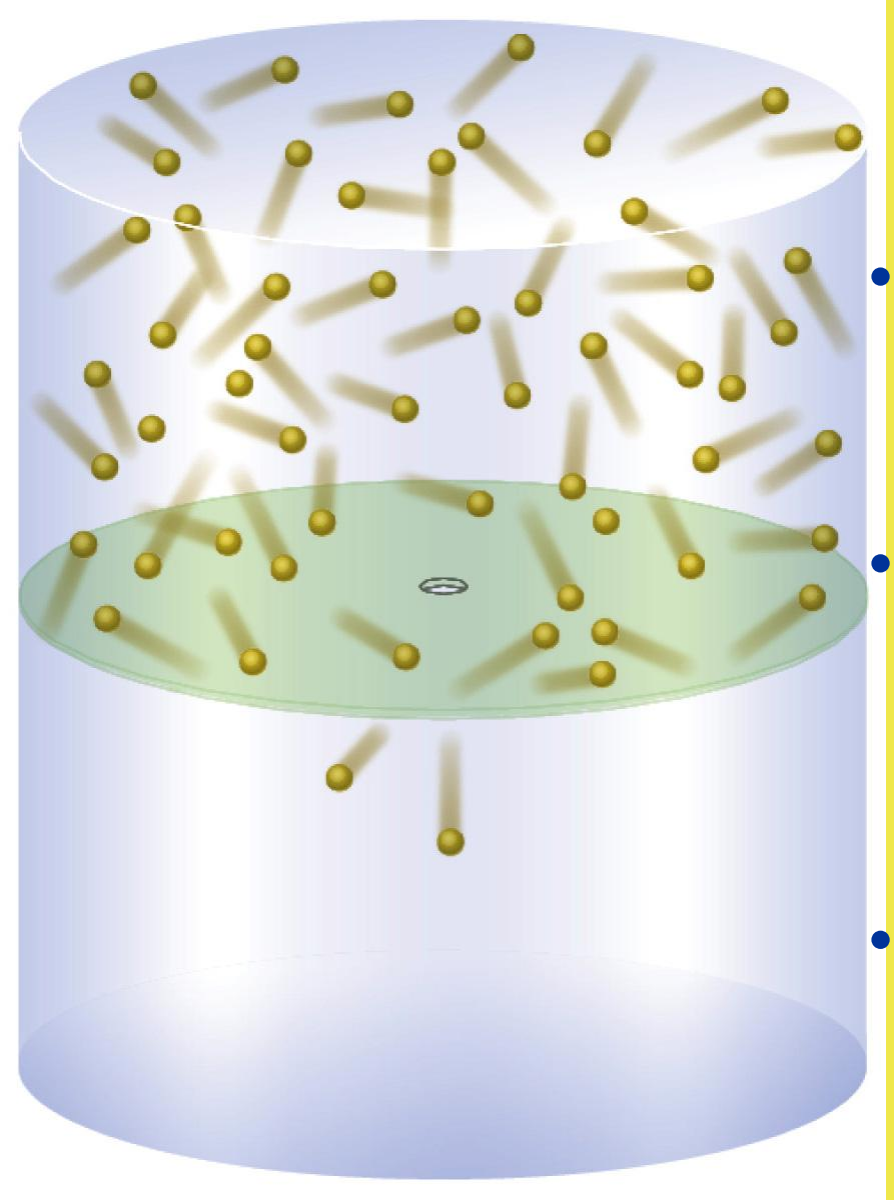
$$\varepsilon = \frac{1}{2} m u^2$$

- Consider two gases at the same temperature: the lighter gas has a higher rms than the heavier gas.
- Mathematically:

$$u = \sqrt{\frac{3RT}{\mathcal{M}}}$$

- The lower the molar mass, $\mathcal{M}$, the higher the rms.





Graham's Law of Effusion

- As kinetic energy increases, the velocity of the gas molecules increases.
- Effusion is the escape of a gas through a tiny hole (a balloon will deflate over time due to effusion).
- The rate of effusion can be quantified.

- Consider two gases with molar masses $\mathcal{M}_1$ and $\mathcal{M}_2$, the relative rate of effusion is given by:

$$\frac{r_1}{r_2} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

- Only those molecules that hit the small hole will escape through it.
- Therefore, the higher the rms the more likelihood of a gas molecule hitting the hole.

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$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \sqrt{\frac{3RT/\mathcal{M}_1}{3RT/\mathcal{M}_2}} = \sqrt{\frac{\mathcal{M}_2}{\mathcal{M}_1}}$$

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- Therefore, the higher the rms the more likelihood of a gas molecule hitting the hole.

Examples – For each pair of gases, determine which will effuse faster, and by how much it will be faster.

1. CH_4 and Xe
2. Cl_2 and N_2
3. F_2 and He

Examples – For each pair of gases, determine which will effuse faster, and by how much it will be faster.

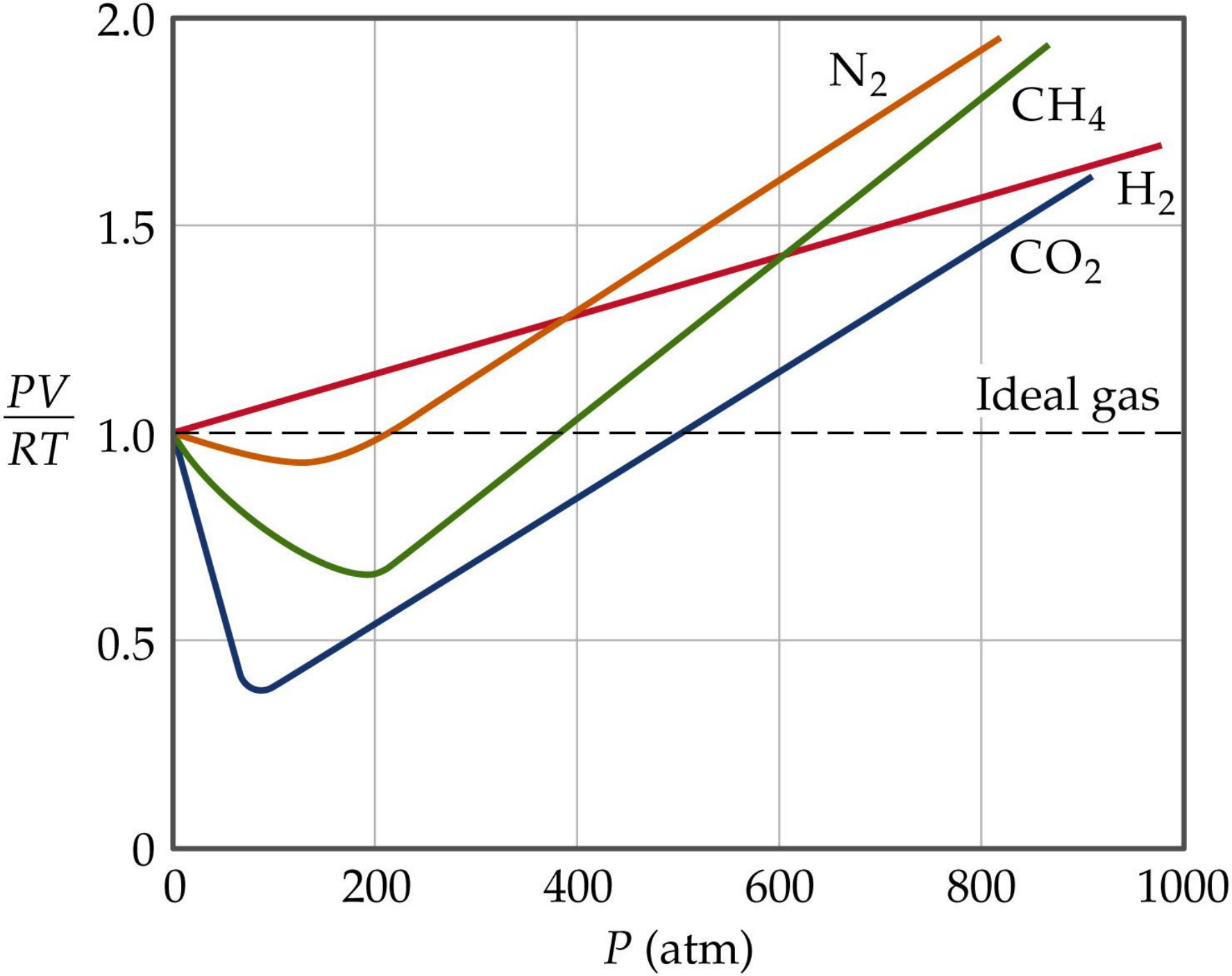
1. CH_4 and Xe 2.8607
2. Cl_2 and N_2 1.59095
3. F_2 and He 3.08027

Real Gases: Deviations from Ideal Behavior

- From the ideal gas equation, we have

$$\frac{PV}{RT} = n$$

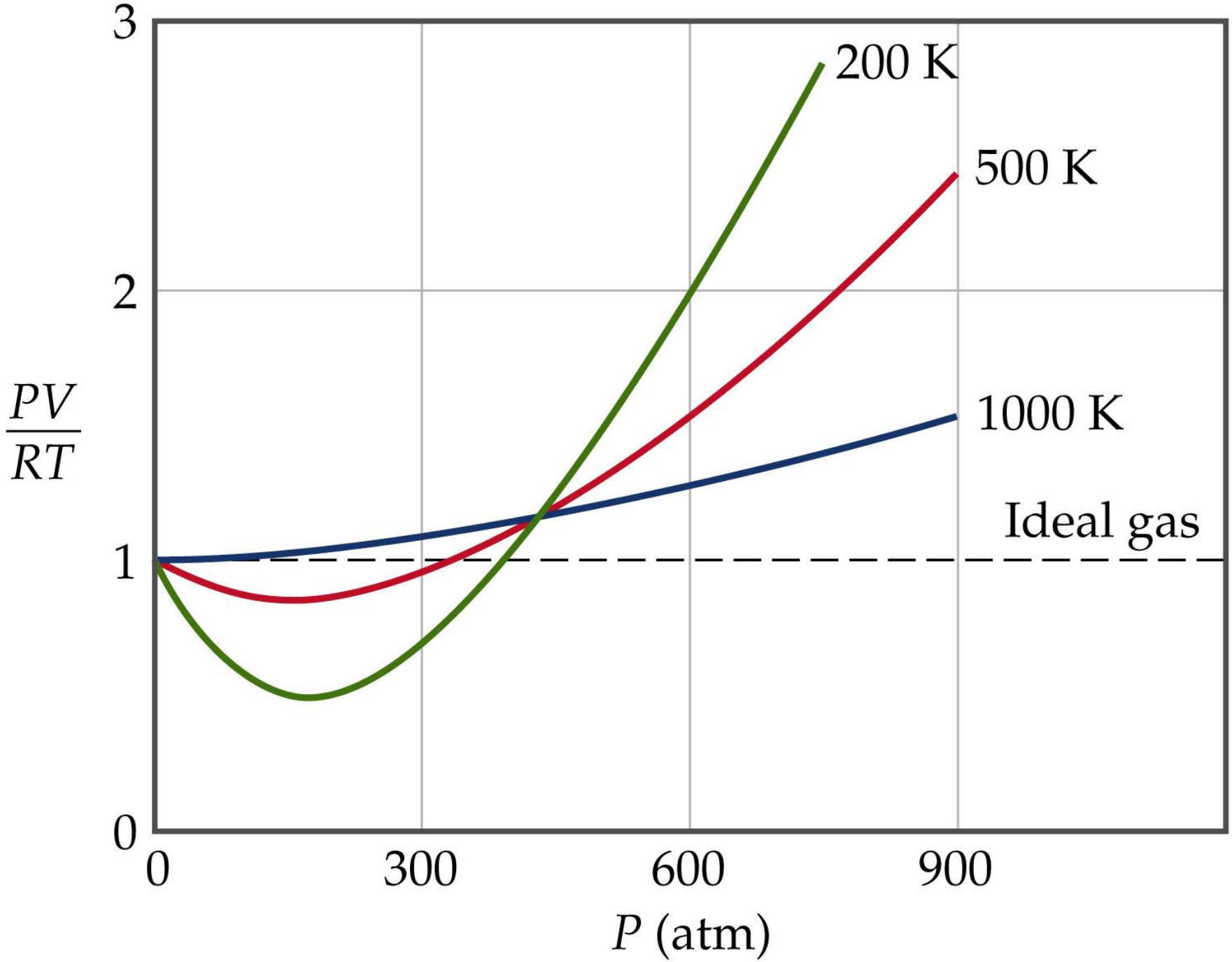
- For 1 mol of gas, $PV/RT = 1$ for all pressures.
- In a real gas, PV/RT varies from 1 significantly.
- The higher the pressure the more the deviation from ideal behavior.


2.0
1.5
1.0
0.5
0
$\frac{PV}{RT}$
N_2
CH_4
H_2
CO_2
Ideal gas
0
200
400
600
800
1000
P (atm)

- From the ideal gas equation, we have

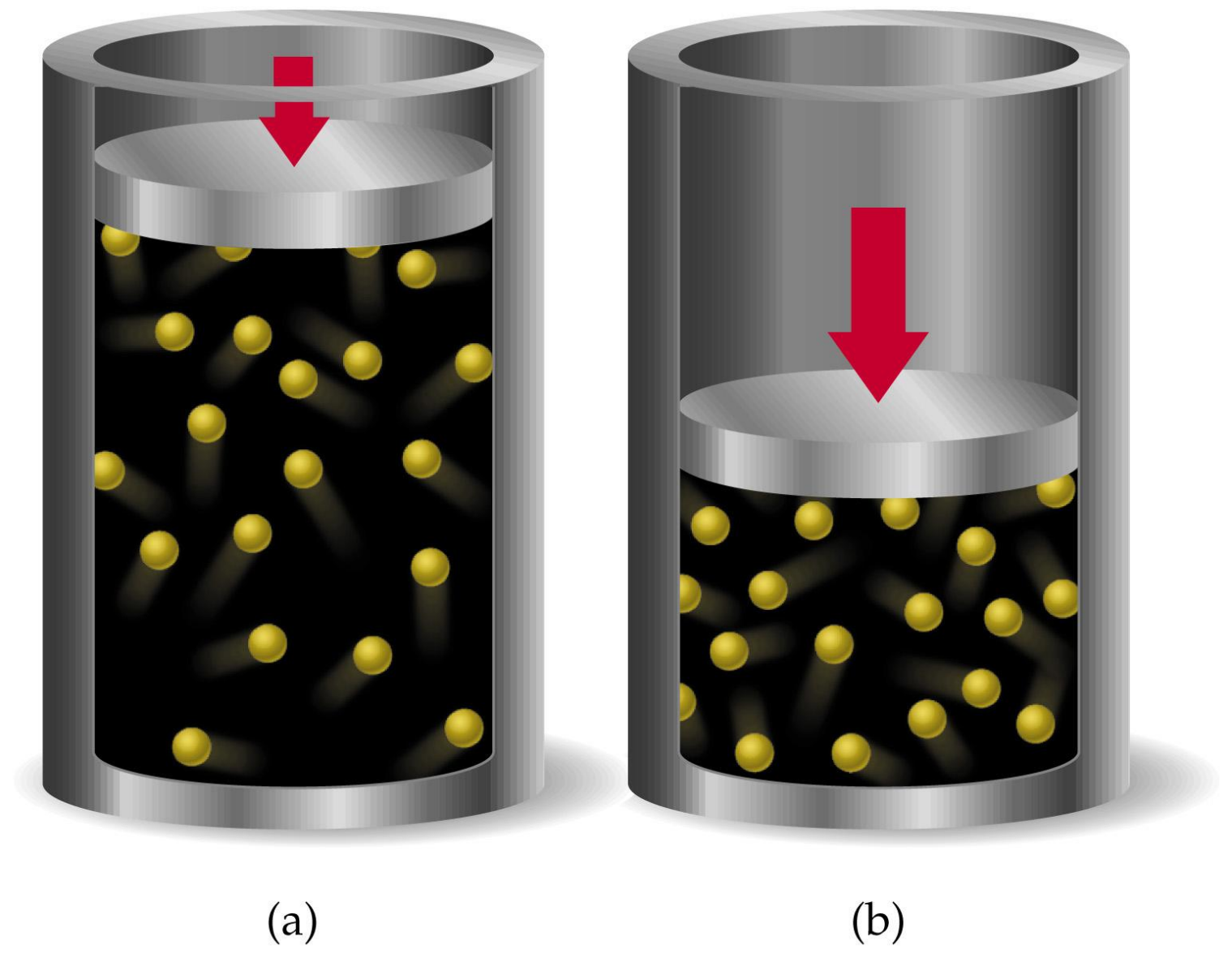
$$\frac{PV}{RT} = n$$

- For 1 mol of gas, $PV/RT = 1$ for all temperatures.
- As temperature increases, the gases behave more ideally.
- The assumptions in kinetic molecular theory show where ideal gas behavior breaks down:
  - the molecules of a gas have finite volume;
  - molecules of a gas do attract each other.


3
2
1
0
$\frac{PV}{RT}$
200 K
500 K
1000 K
Ideal gas
0
300
600
900
P (atm)

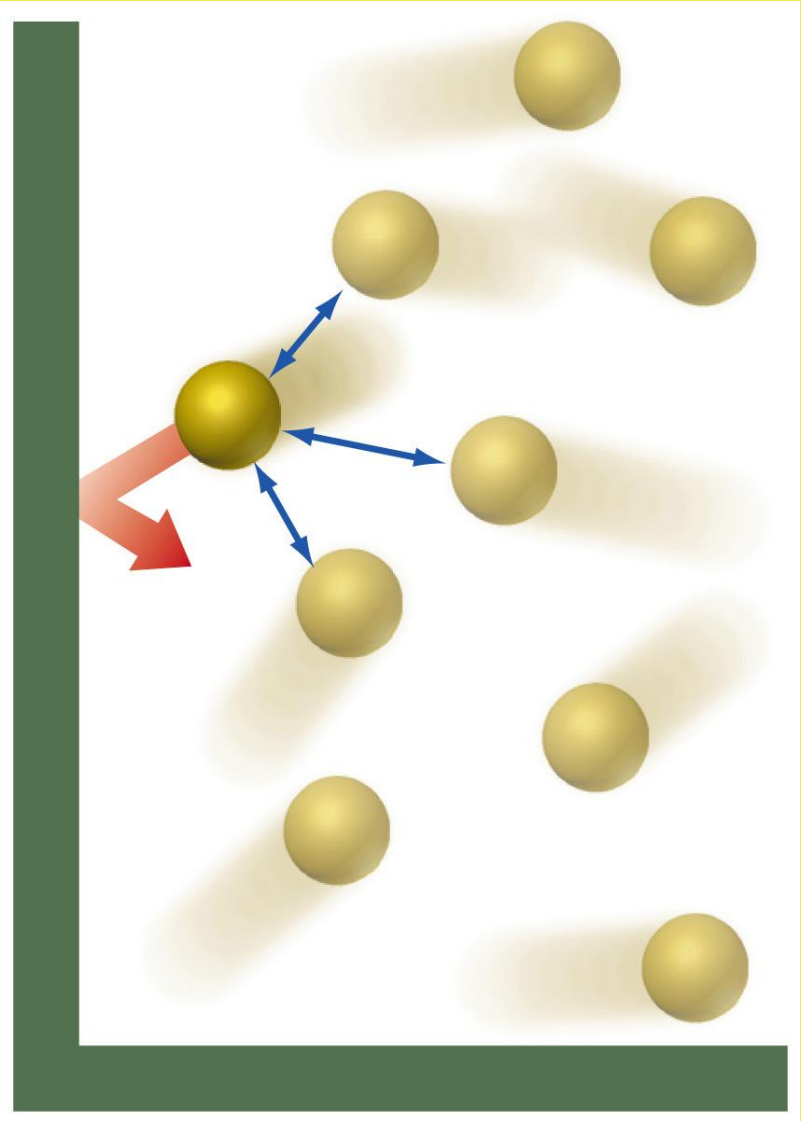
- As the pressure on a gas increases, the molecules are forced closer together.
- As the molecules get closer together, the volume of the container gets smaller.
- The smaller the container, the more space the gas molecules begin to occupy.
- Therefore, the higher the pressure, the less the gas resembles an ideal gas.

- As the gas molecules get closer together, the smaller the intermolecular distance.



- The smaller the distance between gas molecules, the more likely attractive forces will develop between the molecules.
- Therefore, the less the gas resembles and ideal gas.
- As temperature increases, the gas molecules move faster and further apart.
- Also, higher temperatures mean more energy available to break intermolecular forces.

Real Gases: Deviations from Ideal Behavior



- Therefore, the higher the temperature, the more ideal the gas.

The van der Waals Equation

- We add two terms to the ideal gas equation: one to correct for volume of molecules and the other to correct for intermolecular attractions
- The correction terms generate the van der Waals equation:

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

where *a* and *b* are empirical constants.

Real Gases: Deviations from Ideal Behavior

The van der Waals Equation

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Corrects for molecular volume

Corrects for molecular attraction

- General form of the van der Waals equation:

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

TABLE 10.3 van der Waals Constants for Gas Molecules

Substance	a (L^2-atm/mol^2)	b (L/mol)
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
H_2O	5.46	0.0305
CH_4	2.25	0.0428
CO_2	3.59	0.0427
CCl_4	20.4	0.1383