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[TP] The rms speed, $v_{rms} = \sqrt{3RT/M}$, of O_2 at 25°C is about ...
 ("Use units, Luke!" $R = 8.314 \frac{J}{K mol} = 8.314 \frac{kg m^2/s^2}{K mol}$)

9% 1. 250 m/s
 27% 2. 500 m/s
 0% 3. 750 m/s
 0% 4. 1000 m/s
 64% 5. Not sure

738655
 11 of 15




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Lecture 6 CH131 Summer 1 2021

Thursday, June 3, 2021

- Kinetic molecular theory
- Why the gas law does not depend on mass
- Distribution of molecular speeds
- Real gases
- Gas law for real gases: van der Waals equation

Next lecture: Ch10: Solids, liquids and phase transitions




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Kinetic molecular theory

Microscopic model of $P =$
 Identical particles w/ the same mass $m = \frac{M}{N_A}$
 $N_A m = M$
 v_i

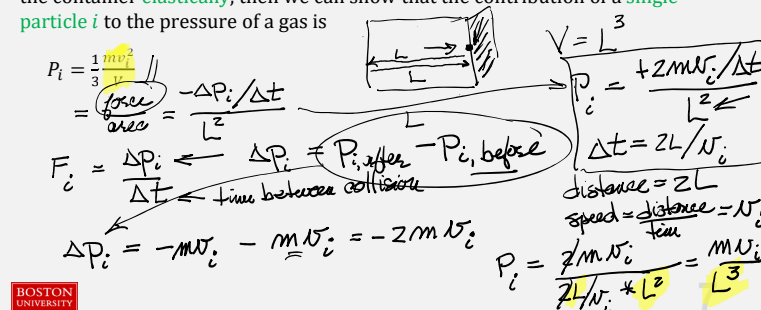


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Kinetic molecular theory

If we assume particles of a gas collide with one another and with the walls of the container **elastically**, then we can show that the contribution of a **single particle i** to the pressure of a gas is



$P_i = \frac{1}{3} \frac{m v_i^2}{V} = \frac{-\Delta p_i / \Delta t}{L^2}$
 $F_i = \frac{\Delta p_i}{\Delta t} \leftarrow \Delta p_i = p_{i, after} - p_{i, before}$
 $\Delta p_i = -m v_i - m v_i = -2m v_i$
 $\Delta t = \frac{2L}{v_i}$
 $P_i = \frac{2m v_i}{2L/v_i * L^2} = \frac{m v_i^2}{L^3}$



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Kinetic molecular theory

If we assume particles of a gas collide with one another and with the walls of the container **elastically**, then we can show that the contribution of a **single particle i** to the pressure of a gas is

$$P_i = \frac{1}{3} \frac{mv_i^2}{V}$$

Note that the units of this expression, $\frac{\text{energy}}{\text{volume}}$, are correct for **pressure**.

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Kinetic molecular theory

If we assume particles of a gas collide with one another and with the walls of the container **elastically**, then we can show that the contribution of a **single particle i** to the pressure of a gas is

$$P_i = \frac{1}{3} \frac{mv_i^2}{V}$$

Note that the units of this expression, $\frac{\text{energy}}{\text{volume}}$, are correct for **pressure**.

The **factor $\frac{1}{3}$** takes into account that motion takes place in **three dimensions**.

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Kinetic molecular theory

The total pressure is the sum of the contributions of the $N = nN_A$ particles of the gas,

$$P = P_1 + P_2 + \dots + P_N = \frac{1}{3} \frac{m}{V} (v_1^2 + v_2^2 + \dots + v_N^2)$$

There are n moles of particles. How many particles.

$$= \frac{1}{3} \frac{mN}{V} (v_1^2 + v_2^2 + \dots + v_N^2)$$

*$N = nN_A$ particles
 $N_A m = \frac{g}{\text{mole}}$*

$$P = \frac{1}{3} \frac{mN}{V} (v_1^2 + v_2^2 + \dots + v_N^2)$$

$$= \frac{1}{3} \frac{M}{V} \rho v_{rms}^2 //$$

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Kinetic molecular theory

The total pressure is the sum of the contributions of the $N = nN_A$ particles of the gas,

$$P = P_1 + P_2 + \dots + P_N = \frac{1}{3} \frac{m}{V} (v_1^2 + v_2^2 + \dots + v_N^2)$$

We can simplify this expression by dividing the **sum of squared speeds** by the **number of particles (N)**,

$$P = \frac{1}{3} \frac{mN}{V} \left(\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N} \right) = \frac{1}{3} \frac{mN}{V} v_{rms}^2$$

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Kinetic molecular theory

The total pressure is the sum of the contributions of the $N = nN_A$ particles of the gas,

$$P = P_1 + P_2 + \dots + P_N = \frac{1}{3} \frac{m}{V} (v_1^2 + v_2^2 + \dots + v_N^2)$$

We can simplify this expression by dividing the **sum of squared speeds** by the **number of particles (N)**,

$$P = \frac{1}{3} \frac{mN}{V} \left(\frac{v_1^2 + v_2^2 + \dots + v_N^2}{N} \right) = \frac{1}{3} \frac{mN}{V} v_{rms}^2$$

The quantity $v_{rms}^2 = \frac{v_1^2 + v_2^2 + \dots + v_N^2}{N}$ is the **mean** (average) of the **squared speeds** of the individual particles.

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Kinetic molecular theory

Comparing the expression for pressure from the **kinetic molecular theory**

$$P = \frac{1}{3} \frac{mN}{V} v_{rms}^2 = \frac{1}{3} \frac{mN_A n}{V} v_{rms}^2 = \frac{1}{3} \frac{Mn}{V} v_{rms}^2$$

to that from the **ideal gas law**,

$$P = \frac{nRT}{V},$$

we get the fundamental connection between **temperature** and the **mean of the squared speeds**,

$$v_{rms}^2 = \frac{3RT}{M} //$$

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Kinetic molecular theory

The square **root** of the **mean** of the **squared** speeds is known the **root-mean-squared speed**,

$$v_{rms} = \sqrt{\frac{3RT}{M}} //$$

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[TP] The rms speed, $v_{rms} = \sqrt{3RT/M}$, of O_2 at $25^\circ C$ is about ...
 ("Use units, Luke!" $R = 8.314 \frac{J}{K mol} = 8.314 \frac{kg m^2/s^2}{K mol}$ $M = 32 g/mol$)

0% 1. 250 m/s
 92% 2. 500 m/s
 0% 3. 750 m/s
 0% 4. 1000 m/s
 8% 5. Not sure

$v_{rms} = \sqrt{3 \times 8.314 \times \frac{kg m^2}{s^2 K mol} \times 298 K} = \sqrt{738655} = 859.7 m/s$

738655

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Kinetic molecular theory

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$R = 8.314 \frac{\text{J}}{\text{K mol}} = 8.314 \frac{\text{kg m}^2/\text{s}^2}{\text{K mol}}$$

Answer: 482 m/s \approx 500 m/s

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[TP] The rms speed of O₂ at 25°C is about 500 m/s. Without using a calculator, use the rms speed of O₂ to estimate that the rms speed of H₂ at the same temperature is about ...

0% 1. 4000 m/s
 100% 2. 2000 m/s
 0% 3. 1000 m/s
 0% 4. 500 m/s
 0% 5. 250 m/s
 0% 6. Not sure

O₂ 32 g/mol
 H₂ 2 g/mol

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$\frac{v_{H_2}}{v_{O_2}} = \frac{\sqrt{\frac{3RT}{M_{H_2}}}}{\sqrt{\frac{3RT}{M_{O_2}}}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} = \sqrt{\frac{32}{2}} = 4$$

v_{H₂} = 4 v_{O₂}

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Why the gas law does not depend on mass

We have seen that the macroscopic behavior of gas pressure is that

$$P = \frac{nRT}{V} = \frac{1}{3} \frac{Mn}{V} v_{rms}^2 = \frac{1}{3} \frac{Mn}{V} \frac{3RT}{M} = \frac{nRT}{V}$$

Why doesn't P depend on molar mass (M)?

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Why the gas law does not depend on mass

We have seen that the microscopic model of gas pressure is that

$$P = \frac{1}{3} \frac{Mn}{V} v_{rms}^2 \text{ where } v_{rms} = \sqrt{\frac{3RT}{M}}$$

Why doesn't P depend on molar mass (M)?

The reason is that root-mean-square speed offsets the apparent mass dependence,

$$P = \frac{1}{3} \frac{Mn}{V} v_{rms}^2 = \frac{1}{3} \frac{Mn}{V} \times \frac{3RT}{M} = \frac{nRT}{V}$$

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Distribution of molecular speeds

The distribution of speeds is a plot of the fraction of particles (y axis) at each speed (x axis).

At 300 K, the rms speed of O₂ is $v_{rms} = 500$ m/s.



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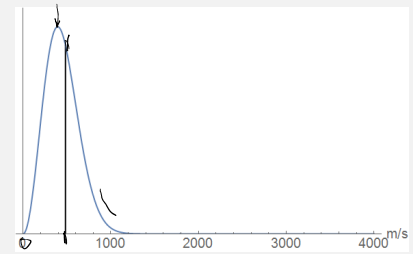

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Distribution of molecular speeds

Here is the distribution of speeds of O₂ at 300 K, from 0 m/s to 4000 m/s, marking the position of v_{rms} on the x axis.

The lowest rms speed is 0 and speeds extend **exponentially** to high values.

Maxwell-Boltzmann distribution

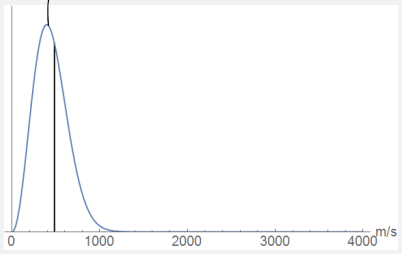

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Distribution of molecular speeds

The means v_{rms} is slightly higher than the most probable speed,

$$v_{mp} = \sqrt{2/3} v_{rms} \approx 0.82 v_{rms}$$



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[TP] Use the rms speed of O₂ at 300 K, $v_{rms} = 500$ m/s. Without a calculator, use this value to find the rms speed of O₂ at 1200 K.

0% 1. 4000 m/s
 15% 2. 2000 m/s
 85% 3. 1000 m/s
 0% 4. 500 m/s
 0% 5. 250 m/s
 0% 6. Not sure

Handwritten notes:

300K
 1200K
 $\frac{N_{1200}}{N_{300}} = \sqrt{\frac{3R \cdot 1200}{3R \cdot 300}} = \sqrt{\frac{1200}{300}} = \sqrt{4} = 2$
 $N_{1200} = 2 N_{300} = 2 * 500 m/s = 1000 m/s$
 733655
 $\frac{1}{9} + \frac{2}{9} + \frac{6}{9} = 1$



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v_{rms} versus temperature

The rms speed of O_2 at 300 K is 500 m/s and the rms speed of O_2 at 1200 K is 1000 m/s. Sketch the distribution of speeds for O_2 at these two temperatures on the same axes, marking the position of the two rms speeds on the x axis.

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v_{rms} versus temperature

The rms speed of O_2 at 300 K is 500 m/s and the rms speed of O_2 at 1200 K is 1000 m/s. Sketch the distribution of speeds for O_2 at these two temperatures on the same axes, marking the position of the two rms speeds on the x axis.

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[TP] Use the rms speed of O_2 at 300 K, $v_{rms} = 500$ m/s. Without a calculator, use this value to find the rms speed of H_2 at 300 K.

- 0% 1. 4000 m/s
- 100% 2. 2000 m/s
- 0% 3. 1000 m/s
- 0% 4. 500 m/s
- 0% 5. 250 m/s
- 0% 6. Not sure

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v_{rms} versus temperature

Add to your sketch the distribution of speeds of H_2 at 300 K.

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v_{rms} versus temperature

Add to your sketch the distribution of speeds of H_2 at 300 K.

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

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Real gases //

While the **ideal gas law** is the same for every gas, there are **two effects** in all **real gases** that are important at **high gas densities** (due to **temperatures close to condensation** or **very high pressures**).

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Real gases

The first effect is due to **gas particles** themselves **taking up space**.

For example, we have seen that at 100°C, the density of $H_2O(g)$ is $0.0327 \frac{mol}{L}$ and the density of $H_2O(l)$ is $0.958 \frac{g}{mL}$. // = $\frac{958g}{L}$

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[TP] The density of $H_2O(g)$ is $0.0327 \frac{mol}{L}$ and the density of $H_2O(l)$ is $0.958 \frac{g}{mL}$.

Calculate how much space is taken up by the water molecules in 1 L of gaseous water at 100°C.

0% 1. 0.0001 L
 100% 2. 0.0006 L
 0% 3. 0.001 L
 0% 4. 0.006 L
 0% 5. 0.01 L
 0% 6. 0.06 L
 0% 7. Not sure //

$$0.0327 \frac{mol}{L} \times 18g \times \frac{1mL}{0.958g} \times \frac{1L}{1000mL}$$

$PV = nRT$

$V = 0.0006 L$

$1L = 0.0006L + \text{empty space}$
 empty space = $1L - 0.0006L$

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Real gases

The density of $\text{H}_2\text{O}(g)$ is $0.0327 \frac{\text{mol}}{\text{L}}$ and the density of $\text{H}_2\text{O}(l)$ is $0.958 \frac{\text{g}}{\text{mL}}$, so the volume taken up by the gaseous water as a liquid would be

$$V_{\text{H}_2\text{O}(l)} = 0.0327 \text{ mol} \frac{18.0 \text{ g}}{\text{mol}} \times \frac{\text{mL}}{0.958 \text{ g}} \times \frac{\text{L}}{1000 \text{ mL}} = 0.000614 \text{ L}$$

This means that

$$\frac{0.000614 \text{ L}}{1 \text{ L}} \times 100\% = 0.06\% \text{ not empty space}$$

of the 1-L volume is taken up by the water molecules,

$$1 \text{ L} = \underbrace{V_{\text{ideal}}}_{V_{\text{ideal}} = \text{empty space}} + V_{\text{H}_2\text{O}(l)}$$

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Real gases

More generally, the volume of the container is expressed as **empty space** (V_{ideal}) plus that taken up by the molecules themselves,

$$V = V_{\text{ideal}} + (bn) \quad 0.0006 \text{ L}$$

Here the parameter **van der Waals b** is the volume taken up by **one mole of the molecules of the substance**.

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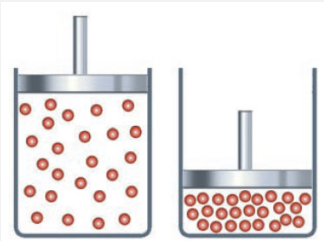
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Real gases

$$V = V_{\text{ideal}} + bn$$

At **high pressures**, the volume of the molecules of a gas (bn) is **no longer negligible** relative to the volume of the container (V).



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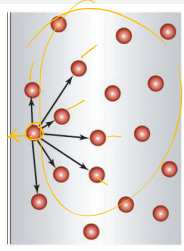
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Real gases

The second effect is due to **attraction of the gas particles for one another**.

This attraction **lessens the impact** of each particle with the container walls and so **reduces the pressure**.



$$\frac{m}{V} \frac{M}{V}$$

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Real gases

The reduction in pressure is proportional to the number of particles hitting the wall and the number of neighboring particles lessening each particle's impact with the wall,

$$P = P_{\text{ideal}} - a \left(\frac{n}{V}\right)^2$$

The parameter van der Waals a is a measure of the intermolecular attraction exerted between particles of the gas.

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Real gases

The ideal gas law relates P_{ideal} and V_{ideal} ,

$$P_{\text{ideal}} V_{\text{ideal}} = nRT$$

Using the expressions $V = V_{\text{ideal}} + bn$ and $P = P_{\text{ideal}} - a \left(\frac{n}{V}\right)^2$, we can rewrite the ideal gas law in terms of actual pressure and the actual container volume,

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

This is known as the van der Waal equation.

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

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Real gases

Computations with the van der Waals equation are usually done by rearranging it for the observed pressure,

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

and using tabulated values of van der Waals a and b .

Gas	Formula	$a / \text{L}^2 \cdot \text{bar} \cdot \text{mol}^{-2}$	$b / \text{L} \cdot \text{mol}^{-1}$
ammonia	NH ₃	4.3044	0.037847
carbon dioxide	CO ₂	3.6551	0.042816
methane	CH ₄	2.3026	0.043067
neon	Ne	0.2167	0.017383
nitrogen	N ₂	1.3661	0.038577
oxygen	O ₂	1.3820	0.031860
propane	C ₃ H ₈	9.3919	0.090494

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Real gases

Computations with the van der Waals equation are usually done by rearranging it for the observed pressure,

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

This expression makes it easier to see that a reduces pressure and b increases pressure, relative to ideal values.

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Working with the van der Waals equation

$$P = \frac{nRT}{v-bn} - a\left(\frac{n}{v}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2 , $a = 6.58 \text{ bar L}^2/\text{mol}^2$ and $b = 0.0562 \text{ L/mol}$. What are the **ideal** and **observed** pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

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Working with the van der Waals equation

$$P = \frac{nRT}{v-bn} - a\left(\frac{n}{v}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2 , $a = 6.58 \text{ bar L}^2/\text{mol}^2$ and $b = 0.0562 \text{ L/mol}$. What are the **ideal** and **observed** pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

$$P_{\text{ideal}} = \frac{nRT}{v} = 31.3 \text{ bar (confirm yourself)}$$

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Working with the van der Waals equation

$$P = \frac{nRT}{v-bn} - a\left(\frac{n}{v}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2 , $a = 6.58 \text{ bar L}^2/\text{mol}^2$ and $b = 0.0562 \text{ L/mol}$. What are the **ideal** and **observed** pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

$$P_{\text{ideal}} = \frac{nRT}{v} = 31.3 \text{ bar (confirm yourself)}$$

$$P = \frac{nRT}{v-bn} - a\left(\frac{n}{v}\right)^2 = 32.5 \text{ bar} - 3.7 \text{ bar} = 28.8 \text{ bar (confirm yourself)}$$

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Working with the van der Waals equation

$$P = \frac{nRT}{v-bn} - a\left(\frac{n}{v}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2 , $a = 6.58 \text{ bar L}^2/\text{mol}^2$ and $b = 0.0562 \text{ L/mol}$. What are the **ideal** and **observed** pressures of 3.00 mol of Cl_2 confined in 4.00 L at 500. K?

$$P_{\text{ideal}} = \frac{nRT}{v} = 31.3 \text{ bar (confirm yourself)}$$

$$P = \frac{nRT}{v-bn} - a\left(\frac{n}{v}\right)^2 = 32.5 \text{ bar} - 3.7 \text{ bar} = 28.8 \text{ bar (confirm yourself)}$$

Since the observed pressure is smaller than the ideal pressure, the **effect of a is more important** than b at 500. K.

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Working with the van der Waals equation

$$P = \frac{nRT}{v-bn} - a\left(\frac{n}{v}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2 , $a = 6.58 \text{ bar L}^2/\text{mol}^2$ and $b = 0.0562 \text{ L/mol}$. What are the **ideal** and **observed** pressures of 3.00 mol of Cl_2 confined in 4.00 L at 3000. K?

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Working with the van der Waals equation

$$p = \frac{nRT}{v-bn} - a\left(\frac{n}{v}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

For Cl_2 , $a = 6.58 \text{ bar L}^2/\text{mol}^2$ and $b = 0.0562 \text{ L/mol}$. What are the **ideal** and **observed** pressures of 3.00 mol of Cl_2 confined in 4.00 L at 3000. K?

$$P_{\text{ideal}} = \frac{nRT}{V} = 187.1 \text{ bar (confirm yourself)}$$

$$P = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 = 195.3 \text{ bar} - 3.7 \text{ bar} = 191.6 \text{ bar (confirm yourself)}$$

Since the observed pressure is larger than the ideal pressure, the **effect of b is more important** than a at 3000. K.

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Working with the van der Waals equation

$$P = \frac{nRT}{v-bn} - a\left(\frac{n}{v}\right)^2 \text{ and } R = 0.08314 \text{ L bar/(K mol)}$$

In general, the effect of b is muted at **low T** and so the effect of a **dominates** there, while for **high T** the effect of b **dominates**.

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