[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.

7% 1. 4000 m/s
68% 2. 2000 m/s
14% 3. 1000 m/s
8% 4. 500 m/s
3% 5. 250 m/s

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149 of 191 1 0

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1

Lecture 11 CH131 Fall 2020

Tuesday, October 20, 2020

- Complete: Distribution of molecular speeds
- Real gases
- Gas law for real gases: van der Waals equation

Ch10: Solids, liquids and phase transitions

- Intermolecular forces (IMF): H-bond, dipole-dipole, London
- IMFs determine relative boiling points

Next lecture: Continue ch10

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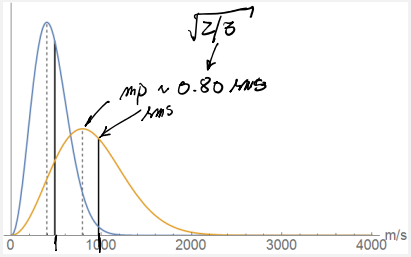
2

u_{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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6

6

[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.

7% 1. 4000 m/s
81% 2. 2000 m/s
7% 3. 1000 m/s
4% 4. 500 m/s
1% 5. 250 m/s

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152 of 191 7 0

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7

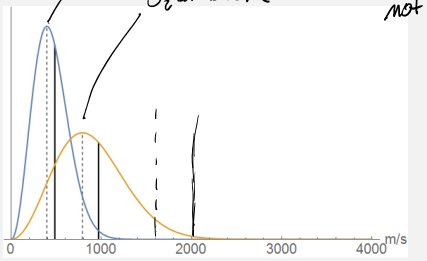
v_{rms} versus temperature

Add to your sketch the distribution of speeds of H_2 at 300 K. ⇒ 2000 m/s

O_2 at 300K

O_2 at 1200K

fewer low speeds
more high speeds
not as many at each speed.



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v_{rms} versus temperature

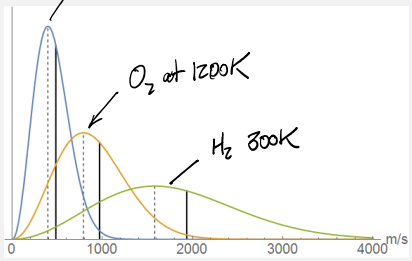
$v = \sqrt{\frac{3RT}{M}}$

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

O_2 at 300K

O_2 at 1200K

H_2 300K



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Real gases

$PV = nRT$

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).

$\frac{n}{V} = \frac{P}{RT}$ ← high P, low T

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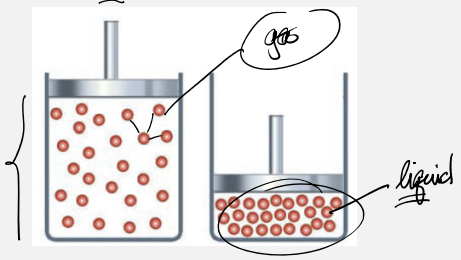
Real gases

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



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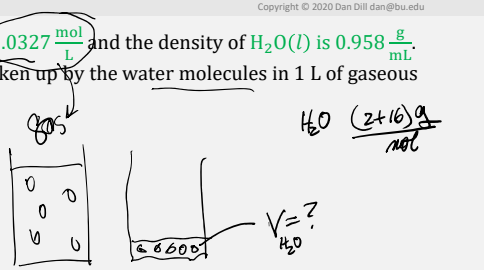
[TP] The density of $H_2O(g)$ is $0.0327\ \frac{\text{mol}}{\text{L}}$ and the density of $H_2O(l)$ is $0.958\ \frac{\text{g}}{\text{mL}}$. Calculate how much space is taken up by the water molecules in 1 L of gaseous water at 100°C.

6% 1. 0.0001 L
29% 2. 0.0006 L
25% 3. 0.001 L
30% 4. 0.006 L
6% 5. 0.01 L
4% 6. 0.06



161 of 191

22

Real gases

The density of $H_2O(g)$ is $0.0327\ \frac{\text{mol}}{\text{L}}$ and the density of $H_2O(l)$ is $0.958\ \frac{\text{g}}{\text{mL}}$, so the volume taken up by the gaseous water as a liquid would be

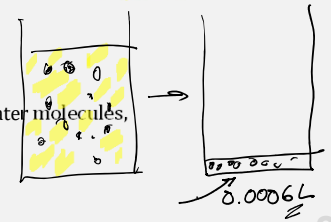
$$V_{H_2O(l)} = 0.0327\ \text{mol} \times \frac{18.0\ \text{g}}{\text{mol}} \times \frac{\text{mL}}{0.958\ \text{g}} \times \frac{\text{L}}{1000\ \text{mL}} = 0.000614\ \text{L}$$

This means that

$$\frac{0.000614\ \text{L}}{1\ \text{L}} \times 100\% = 0.06\%$$

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

$$1\ \text{L} = V_{\text{ideal}} + V_{H_2O(l)}.$$



23

Real gases

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

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

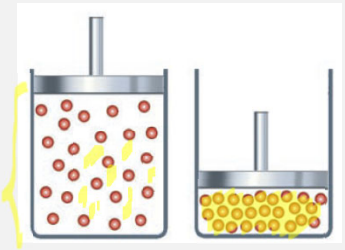
Here the parameter van der Waals b is the volume taken up by one mole of the molecules of the substance.

24

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).

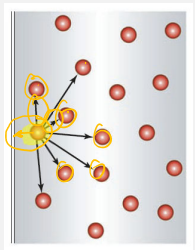


25

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.



P is reduced in proportion to # of particles hitting the wall $\left(\frac{n}{V}\right)$ and # of particle holding back the particles hitting the wall $\left(\frac{n}{V}\right)$

26

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,

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

a has units pressure / (density)^2

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

27

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

$b=0$ (particles are points with no volume)

$a \approx 0$ (particles do not attract one another)

$V_{ideal} = V - bn$

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

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

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

$\frac{a}{b}$ $\frac{n}{V}$

28

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/L²·bar·mol⁻²	b/L·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_3H_8	9.3919	0.090494

29

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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30

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, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ 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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31

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, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ 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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32

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, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ 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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33

Working with the van der Waals equation

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

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

$P_{ideal} = \frac{nRT}{V} = 31.3$ 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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34

Working with the van der Waals equation

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

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ 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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35

Working with the van der Waals equation

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

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

$P_{ideal} = \frac{nRT}{V} = 187.1$ 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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36

Why intermolecular forces (IMF)?

We know from the van der Waals equation that gases attract one another.

Indeed, if they did not, they would not liquify.

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41

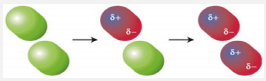
Intermolecular forces: electrical stickiness!

Molecules attract one another, because of the attraction of opposite electrical charges.

The most specific and strongest IMF is "hydrogen bonding": X—H···Y

More common and of intermediate strength IMF is "dipole-dipole attraction":

Always present and weakest IMF is "temporary dipole attraction" ("London force"):



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42

42

Hydrogen bonding

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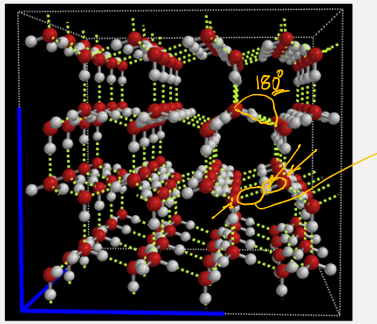
43

43

Ice and water



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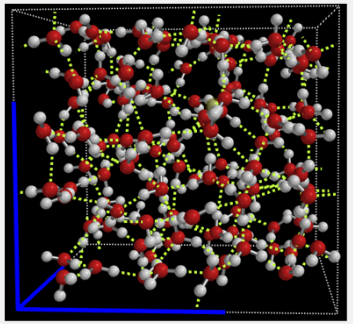
44

44

Ice and water



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45

45

Hydrogen bonds are longer than typical bonds

N—H - - - :N—	O—H - - - :N—	F—H - - - :N—
N—H - - - :O—	O—H - - - :O—	F—H - - - :O—
N—H - - - :F—	O—H - - - :F—	F—H - - - :F—

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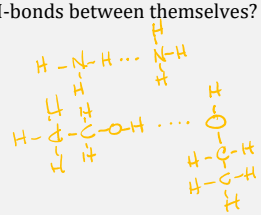
46

46

[TP] Which of the following cannot form H-bonds between themselves?

9% 1. Ammonia, NH_3
6% 2. Methanol, CH_3OH
7% 3. Ethanol, CH_3CH_2OH
13% 4. Dimethyl ether, CH_3OCH_3
6% 5. 1 and 3
19% 6. 1 and 4
12% 7. 2 and 4
28% 8. All of the above can form hydrogen bonds with themselves



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164 of 191

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49