Lecture 7 CH131 Summer 1

Wednesday, June 3, 2020

- 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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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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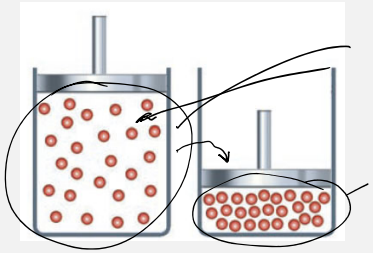
Real gases

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



99.94% empty + 0.06% contains

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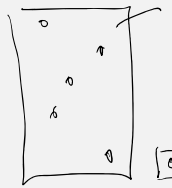
[TP] The density of $H_2O(g)$ is $0.0327\,\frac{\text{mol}}{\text{L}}$ and the density of $H_2O(l)$ is $0.958\,\frac{\text{g}}{\text{mL}}$.
Calculate how much space is taken up by the water molecules in 1 L of gaseous water at 100°C.

6% 1. 0.0001 L
44% 2. 0.0006 L
38% 3. 0.001 L
6% 4. 0.006 L
6% 5. 0.01 L
0% 6. 0.06



empty space + space filled by water molecules = total volume

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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

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

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,

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

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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,

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

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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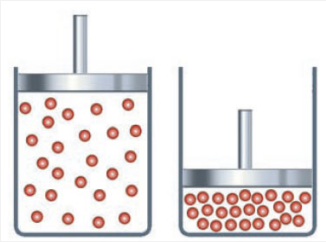
Real gases

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

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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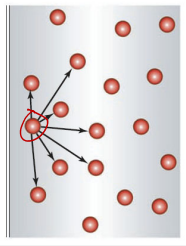
Real gases

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.



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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,

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

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

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.

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

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 L²/mol² 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?

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

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)

$P = \frac{nRT}{V - 0.0562\,L/mol \cdot 3.00\,mol} - 6.58\,\frac{bar\,L^2}{mol^2}\left(\frac{3.00\,mol}{4.00\,L}\right)^2$

$=$

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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)

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

b makes pressure higher

a makes pressure lower

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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)

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

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

$P_{ideal} =$

$P =$

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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?

$P_{ideal} = \frac{nRT}{V} = 187$ bar (confirm yourself)

$P = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 = 195.3$ bar $- 3.7$ bar $= 191.6$ 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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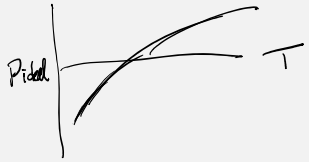
Working with the van der Waals equation

$P = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2$ and $R = 0.08314$ 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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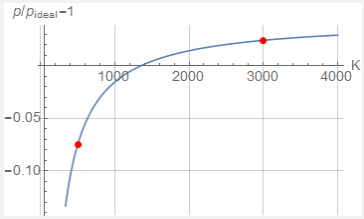
Working with the van der Waals equation

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

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.

For 3.00 mol of Cl_2 confined in 4.00 L, here is $\frac{P}{P_{ideal}} - 1$ versus T.



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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/(L mol)

For Cl_2, $a = 6.58$ bar L^2/mol^2 and $b = 0.0562$ L/mol. What is the observed and ideal pressures of 8.00 mol of Cl_2 confined in 4.00 L at 27 °C? Use

$P_{ideal} = \frac{nRT}{V} = 49.9$ bar

$P = \frac{nRT}{V-bn} - a\left(\frac{n}{V}\right)^2 = 56.2$ bar $- 26.3$ bar $= 29.9$ bar

Since the observed pressure is smaller than the ideal pressure, the effect of a is more important than b at 27 °C

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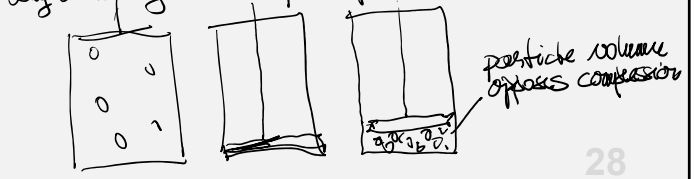
Problem 7e:9.49 and 8e:9.51

$a = 3.640\ \text{L}^2\text{bar/mol}^2$

$b = 0.04267\ \text{L/mol}$

49. Using (a) the ideal gas law and (b) the van der Waals equation, calculate the pressure exerted by 50.0 g carbon dioxide in a 1.00-L vessel at 25°C. Do attractive or repulsive forces dominate?



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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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Intermolecular forces: electrical stickiness!

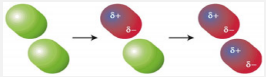
Molecules attract one another, because of the attraction of opposite electrical charges.

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"):

dispersion
van der Waals



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Hydrogen bonding

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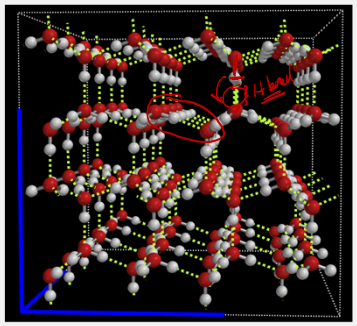
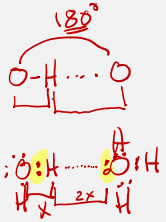
Ice and water





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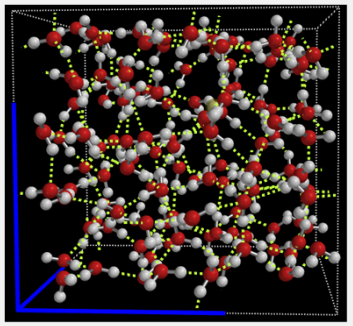
Ice and water



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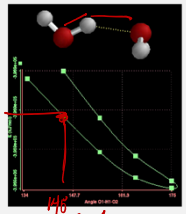
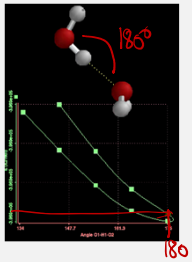
Hydrogen bond angle is 180°

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—





Strength

140° Angle

180

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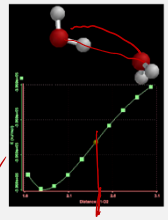
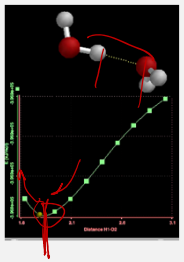
Hydrogen bonds are longer than typical bonds

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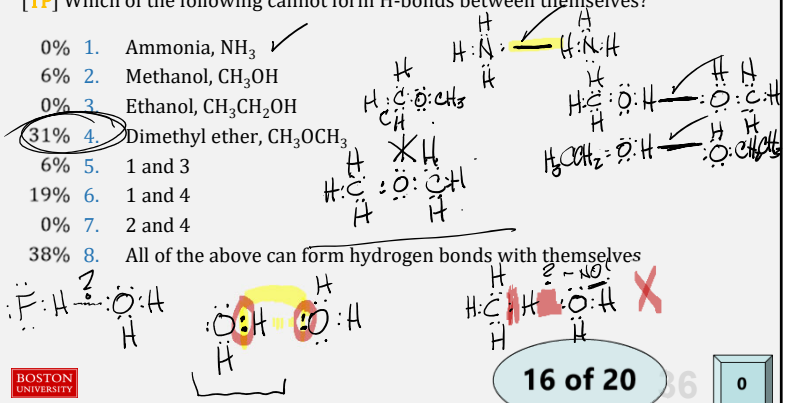
[TP] Which of the following cannot form H-bonds between themselves?

0% 1. Ammonia, NH_3
6% 2. Methanol, CH_3OH
0% 3. Ethanol, CH_3CH_2OH
31% 4. Dimethyl ether, CH_3OCH_3
6% 5. 1 and 3
19% 6. 1 and 4
0% 7. 2 and 4
38% 8. All of the above can form hydrogen bonds with themselves



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Dipole-dipole attraction

Molecules must be "polar"

What makes a molecule polar is unequal sharing of electron clouds.

Sharing tendency is proportional to electronegativity difference.

The greater the difference of electronegativities,
the more unequal the sharing,
the more polar the shared electron cloud.

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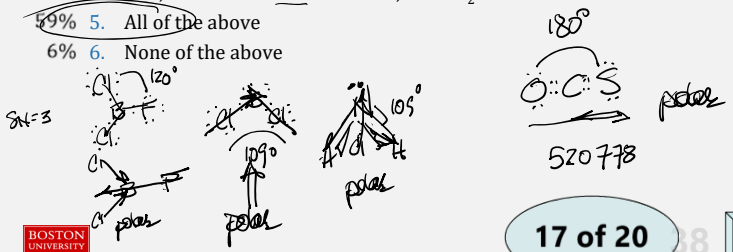
[TP] Which of the following has dipole-dipole IMFs.

0% 1. $BFCl_2$, whose shape is trigonal-planar, like that of BF_3
12% 2. SCl_2, which is a bent molecule, like H_2O
18% 3. NH_2Cl, whose shape is trigonal-pyramidal, like that of NH_3
6% 4. OCS, which is a linear molecule, like CO_2
59% 5. All of the above
6% 6. None of the above



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Instantaneous dipoles → London forces

When one atom encounters another closely, the electrical repulsion between the electron clouds is similar to mismatched (off-resonance) interaction of light and matter.

The result is the electron clouds of all atoms always quiver slightly.

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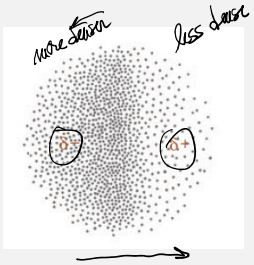
Instantaneous dipoles → London forces

This quivering means that electron clouds are momentarily lopsided, with the result that atom have momentary electrical dipoles.



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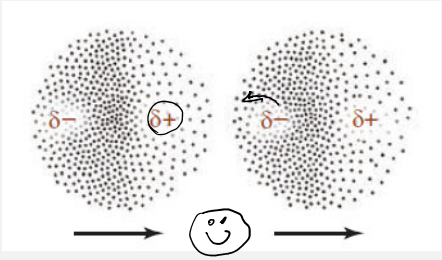
Instantaneous dipoles → London forces

Should another atom pass nearby, the momentary dipole will induce a dipole in the neighboring atom.



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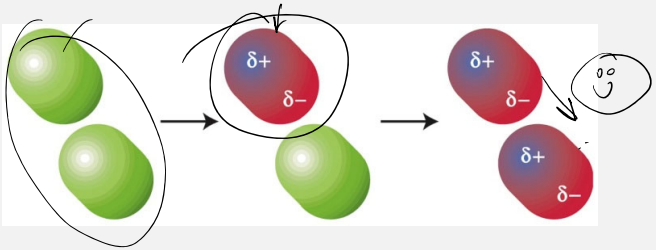
Instantaneous dipoles → London forces

The net result is that electron clouds on neighboring atoms (and molecules) attract one another, due to the London force.



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Relative boiling points

Boiling means particles overcome attraction to their neighbors and depart the liquid.

Relative boiling points reflect relative strength of intermolecular forces …

- London (dispersion)
- Dipole-dipole interaction
- Hydrogen bonding

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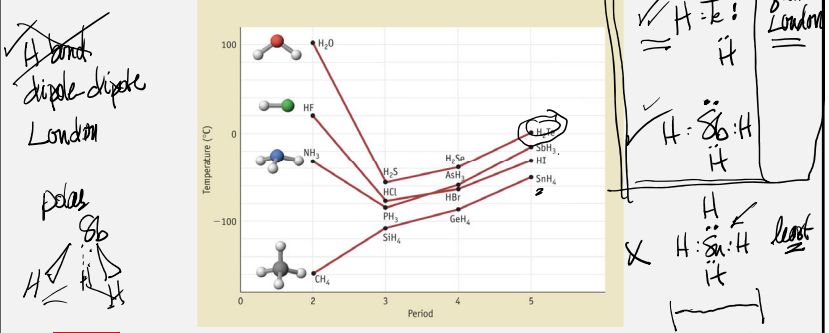
Why is $SnH_4 < SbH_3 < TeH_2$?



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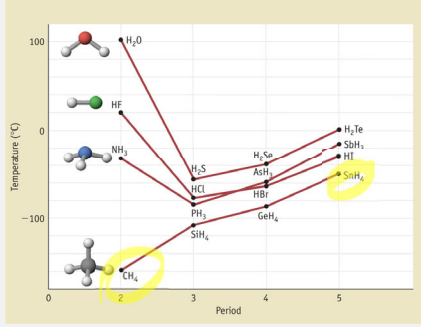
Why is $CH_4 < SiH_4 < GeH_4 < SnH_4$?



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