Lecture 3

Spring 2022

General Chemistry II

Chem 102

- Dalton's Law
- Kinetic Molecular Theory
- Diffusion & Effusion
- Real Gases

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Dalton's Law

Assuming ideal behavior

For a **mixture** of gases in a container, the **total pressure** exerted is the sum of the pressures that each gas would exert if it were alone"

$$P_{Total} = P_1 + P_2 + P_3 + \ldots\ldots\ldots$$

$$= \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \ldots\ldots\ldots$$

$$= (n_1 + n_2 + n_3 + \ldots\ldots\ldots)\frac{RT}{V} = \frac{n_{Total} RT}{V}$$

- P is <u>not affected</u> by the gas identity (composition)
- The gas particle's volume is not important
- The gas intermolecular forces are not important.

Exercise

Mixtures of helium and oxygen can be used in scuba diving tanks to help prevent "the bends." For a particular dive, 46 L He at 25°C and 1.0 atm and 12 L O_2 at 25°C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure in the tank at 25°C.

Solution

$$n_{He} = \frac{(1.0\, atm)(46\, L)}{(0.08206\, L\, .\, atm/K\, .\, mol)(298\, K)} = 1.9\, mol$$

$$n_{O_2} = \frac{(1.0\, atm)(12\, L)}{(0.08206\, L\, .\, atm/K\, .\, mol)(298\, K)} = 0.49\, mol$$

Calculate the partial pressure for each gas in the tank

$$P_{He} = \frac{(1.9\ \text{mol})(0.08206\ L\,.\,atm/K\,.\,mol)(298\ K)}{(5\ L)}$$

$$= 9.3\ atm$$

$$P_{O_2} = \frac{(0.49\ \text{mol})(0.08206\ L\,.\,atm/K\,.\,mol)(298\ K)}{(5\ L)}$$

$$= 2.4\ atm$$

$$\boxed{P_T = P_{He} + P_{O_2} = 9.3 + 2.4 = 11.7\ atm}$$

Mole fraction, χ

The ratio of the number of moles of a given component in a mixture to the total number of moles in the mixture.

$$\chi_1 = \frac{n_1}{n_T} = \frac{n_1}{n_1 + n_2 + n_3 + \ldots\ldots}$$

$$= \frac{\left({}^{V}/_{RT}\right) P_1}{\left({}^{V}/_{RT}\right)(P_1 + P_2 + P_3 + \ldots\ldots)}$$

Mole fraction, χ

$$\chi_1 = \frac{P_1}{(P_1 + P_2 + P_3 + \ldots\ldots)} = \frac{P_1}{P_T}$$

- The mole fraction of each component in a mixture of ideal gases is directly related to its partial pressure

$$\boxed{\chi_2 = \frac{n_2}{n_T} = \frac{P_2}{P_T}}$$

$$\boxed{\sum_i \chi_\mathrm{i} = 1}$$

Exercise

- The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present at 25°C?

Solution

$$\boxed{\chi_{\mathrm{O}_2} = \frac{P_{O_2}}{P_T} = \frac{156\ torr}{743\ torr} = 0.210}$$

Homework

A rigid 9.50 L flask contained a mixture of 3.00 moles of hydrogen (H_2) gas, 1.00 moles of oxygen (O_2) gas, and enough neon (Ne) gas so that the partial pressure of neon in the flask was 3.00 atm. The temperature was 27°C.

1) Calculate the total pressure in the flask.
2) Calculate the mole fraction of oxygen in the flask.
3) Calculate the density in (g mL^{-1}) of the mixture in the flask
4) The gas mixture is ignited by a spark and the reaction below occurs until one of the reactants is totally consumed.

$$O_2(g) + 2H_2(g) \rightarrow 2H_2O(g)$$

Give the mole fraction of all species present in the flask at the end of the reaction.

Kinetic Molecular Theory (KMT)

- A gas is composed of a large number of small (relative to distance between them) particles that behave like hard (point masses: its size, shape, and structure are irrelevant), spherical objects—have negligible volume

- The particles are in constant random (straight-line) motion involving frequent elastic "particle's kinetic energy is not lost" collisions with each other and with the walls of the container (origin of pressure)

- Attractive and repulsive forces between molecules are negligible.

- The average kinetic energy of gas particles is directly proportional only to the absolute "Kelvin" temperature of the gas.

KMT & ideal gas laws are compatible

Boyle's Law

A decrease in volume means that the gas particles will hit the wall more often, thus increasing pressure

$$\boxed{P = nRT\left(\frac{1}{V}\right)}$$

Pressure and Temperature

When a gas temperature increases, the speeds of its particles increase; the particles hit the wall with greater force and greater frequency. Since the volume remains the same, this would result in increased gas pressure

$$\boxed{P = \left(\frac{nR}{V}\right)T}$$

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Charles's Law

If the gas Temp. increases, the particles' speed increases; thus they hit the walls more often and with more force. The only way to keep the pressure constant in this situation is to increase the volume of the container.

$$\boxed{V = \left(\frac{nR}{P}\right) T}$$

Avogadro's Law

The increase in the number of gas particles at the same temperature would cause the pressure to increase if the volume was constant. The only way to return the pressure to its original value is to increase the volume.

$$\boxed{V = \left(\frac{RT}{P}\right) n}$$

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Dalton’s Law

KMT assumes that all gas particles are independent of each other and that the volumes of the individual particles are unimportant. Thus the identities of the gas particles do not matter.

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Root Mean Square Velocity

If $\overline{u^2}$ is the average of the square of the velocities of the particles, The quantity ${}^1\!/_2\, m\overline{u^2}$ will represent the average kinetic energy of a gas particle.

The **average kinetic energy** for a mole of gas particles

$$\boxed{(KE)_{avg} = N_A \left({}^1\!/_2\, m\overline{u^2}\right)}$$

$N_A m = M$ Mass of a mole of the gas (kg)

N_A: Avogadro’s number, m: mass (kg) of each particle

Root Mean Square Velocity

- $\sqrt{\overline{u^2}}$ is also called "root mean square velocity" u_{rms}:

$$\boxed{u_{rms} = \sqrt{\overline{u^2}}}$$

$$\boxed{(KE)_{avg} = {}^{3}\!/_{2}\,RT = N_A\left({}^{1}\!/_{2}\,m\overline{u^2}\right)}$$

$$N_A m = M$$

$$\boxed{u_{rms} = \sqrt{\frac{3RT}{M}}}$$

1 J = 1 kg m²/s²

R= 8.3145 J/K.mol

- For a large number of molecules moving in random directions:

⇨

$$\boxed{\mathrm{PV} = \frac{1}{3}\mathrm{nN_A m}\overline{\mathrm{u}^2}}$$

- However $\mathrm{(KE)_{avg}} = \mathrm{N_A}\left({}^{1}/_{2}\,\mathrm{m}\overline{\mathrm{u}^2}\right)$

⇨

$$\boxed{\begin{aligned}\mathrm{PV} &= \frac{1}{3}\mathrm{nN_A m}\overline{\mathrm{u}^2} = \frac{2}{3}\mathrm{nN_A}\left(\frac{1}{2}\mathrm{m}\overline{\mathrm{u}^2}\right)\\ &= \frac{2}{3}\mathrm{n(KE)_{avg}}\end{aligned}}$$

$$\boxed{\frac{\mathrm{PV}}{\mathrm{n}} = \frac{2}{3}\mathrm{(KE)_{avg}}}$$

⇨

$$\boxed{\frac{\mathrm{PV}}{\mathrm{n}} \propto \mathrm{T} \rightarrow \frac{\mathrm{PV}}{\mathrm{n}} = \mathrm{R\,T}}$$

$$\boxed{\frac{PV}{n} = \frac{2}{3}(KE)_{avg}} \qquad \boxed{(KE)_{avg} = \frac{3}{2}RT} \qquad \boxed{\frac{PV}{n} = RT}$$

Meaning of Temp.: The Kelvin temperature is an index of the random motions of the particles of the gas.

$$\boxed{PV = \frac{1}{3}nN_A m\overline{u^2}} \qquad \boxed{\frac{PV}{n} = RT} \Rightarrow \boxed{\overline{u^2} = \frac{3RT}{N_A m}}$$

$$\sqrt{\overline{u^2}} = u_{rms} = \sqrt{\frac{3RT}{N_A m}} = \sqrt{\frac{3RT}{M}}$$

Exercise

- Calculate the root mean square velocity for the atoms in a sample of helium gas at 25°C.

Solution

$$\mathrm{M} = 4.0\,\frac{\mathrm{g}}{\mathrm{mol}} \times \frac{1\ \mathrm{kg}}{1000\ \mathrm{g}} = 4.0 \times 10^{-3}\,\frac{\mathrm{kg}}{\mathrm{mol}}$$

$$\mathrm{u_{rms}} = \sqrt{\frac{3\mathrm{RT}}{\mathrm{M}}} = \sqrt{\frac{3\left(\frac{8.314\ \mathrm{J}}{\mathrm{K\ mol}}\right)(298\ \mathrm{K})}{\left(4.0 \times 10^{-3}\,\frac{\mathrm{kg}}{\mathrm{mol}}\right)}}$$

$$= \sqrt{1.86 \times 10^{6}\,\frac{\mathrm{J}}{\mathrm{kg}}} = \sqrt{1.86 \times 10^{6}\,\frac{\mathrm{kg\ m^2}}{\mathrm{kg\ s^2}}}$$

$$= \frac{1.36 \times 10^{3}\mathrm{m}}{\mathrm{s}}$$

Exercise

- At the same temperature, compare U_{rms} H_2 with U_{rms} O_2

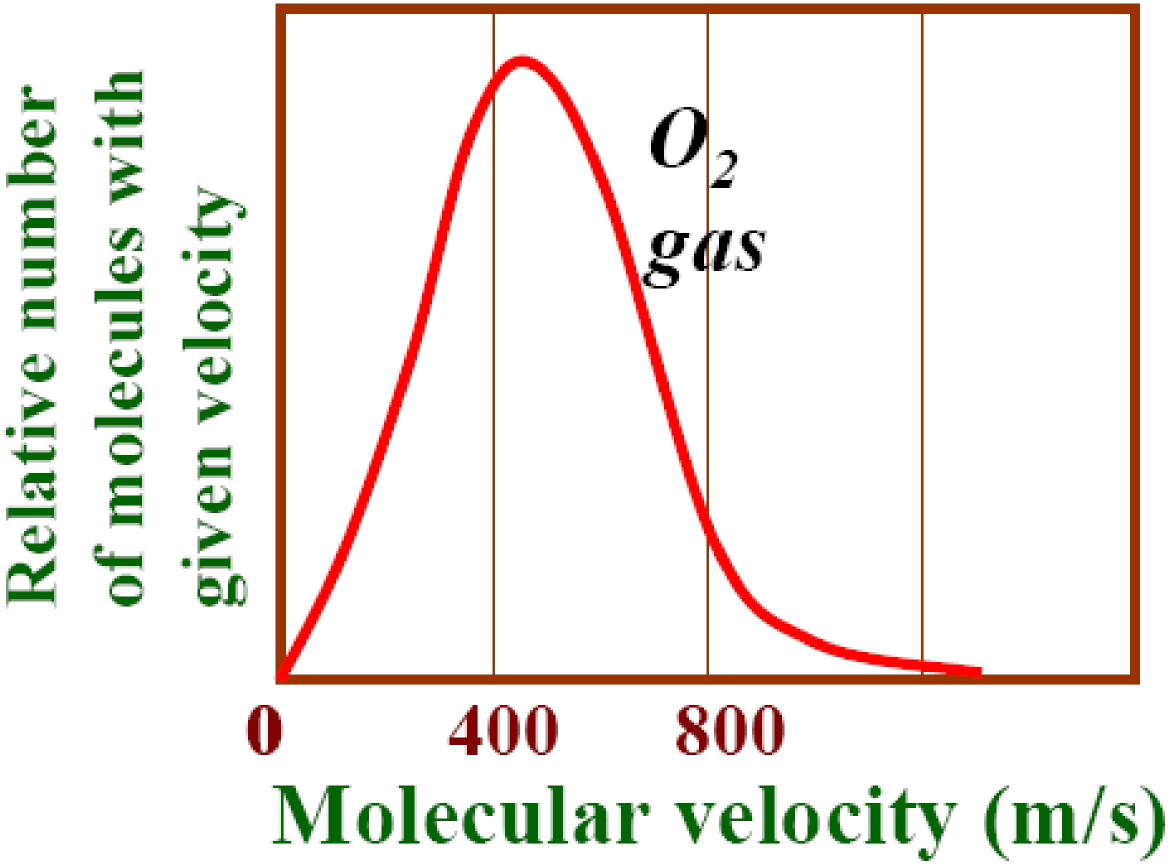
Solution

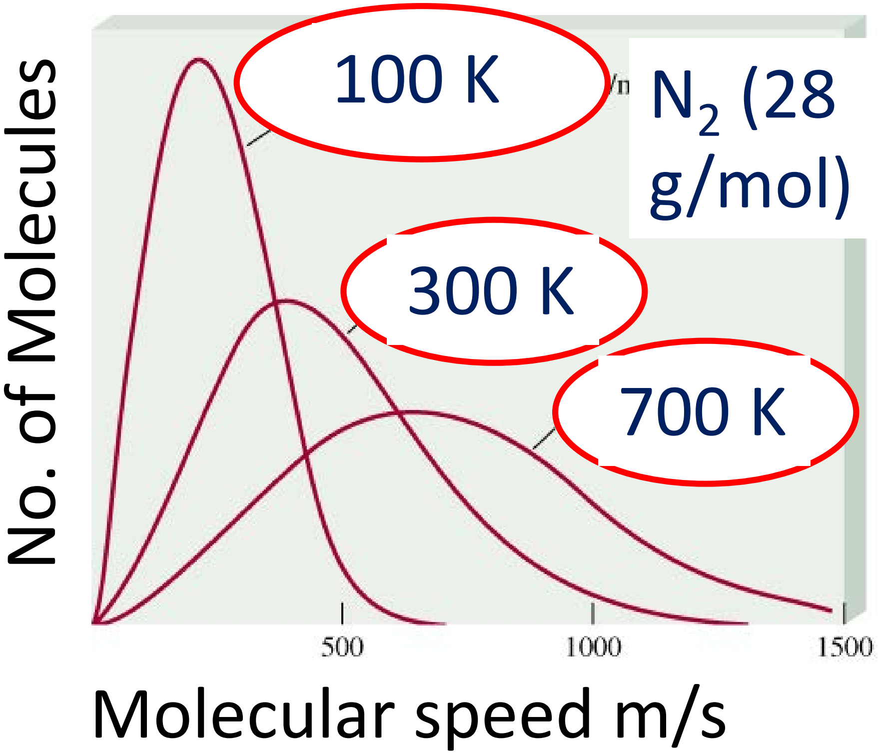
$$\frac{u_{\mathrm{rms}}(H_2)}{u_{\mathrm{rms}}(O_2)} = \frac{\sqrt{\frac{3RT}{M_{H_2}}}}{\sqrt{\frac{3RT}{M_{O_2}}}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}} = \sqrt{\frac{32}{2}} = 4$$

Hydrogen moves 4 times faster than oxygen

Mean free Path

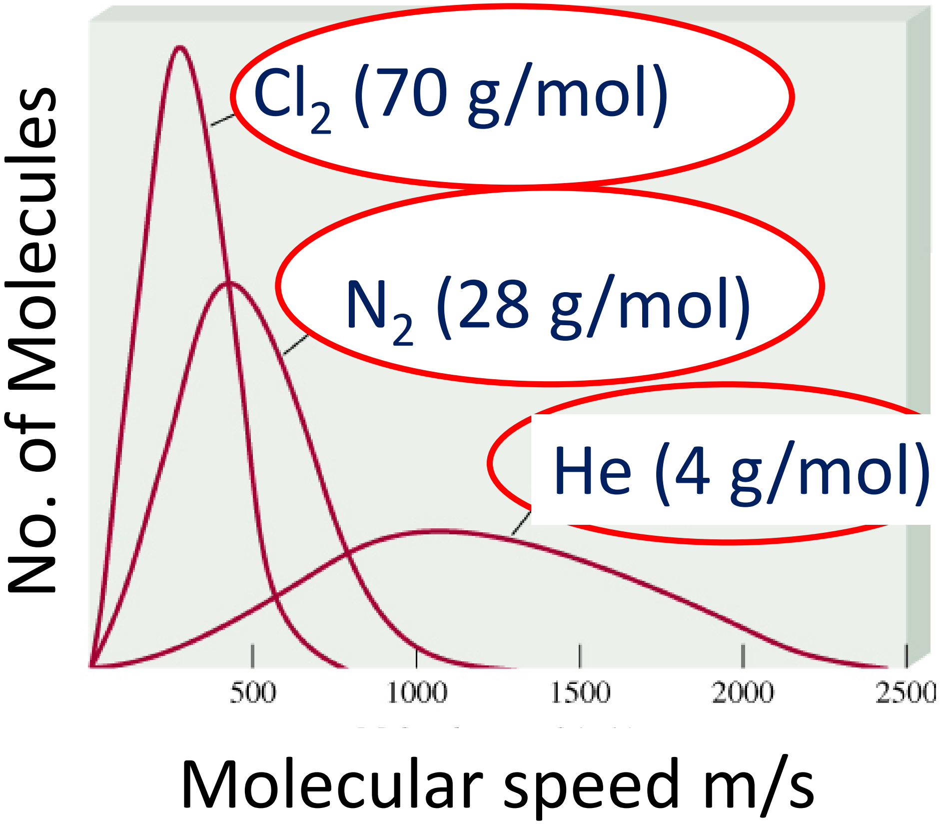
It is the average distance a particle travels between collisions in a particular gas sample.





The distribution of speeds for nitrogen gas molecules at three different temperatures

The distribution of speeds of three different gases at the same temperature T=300 K



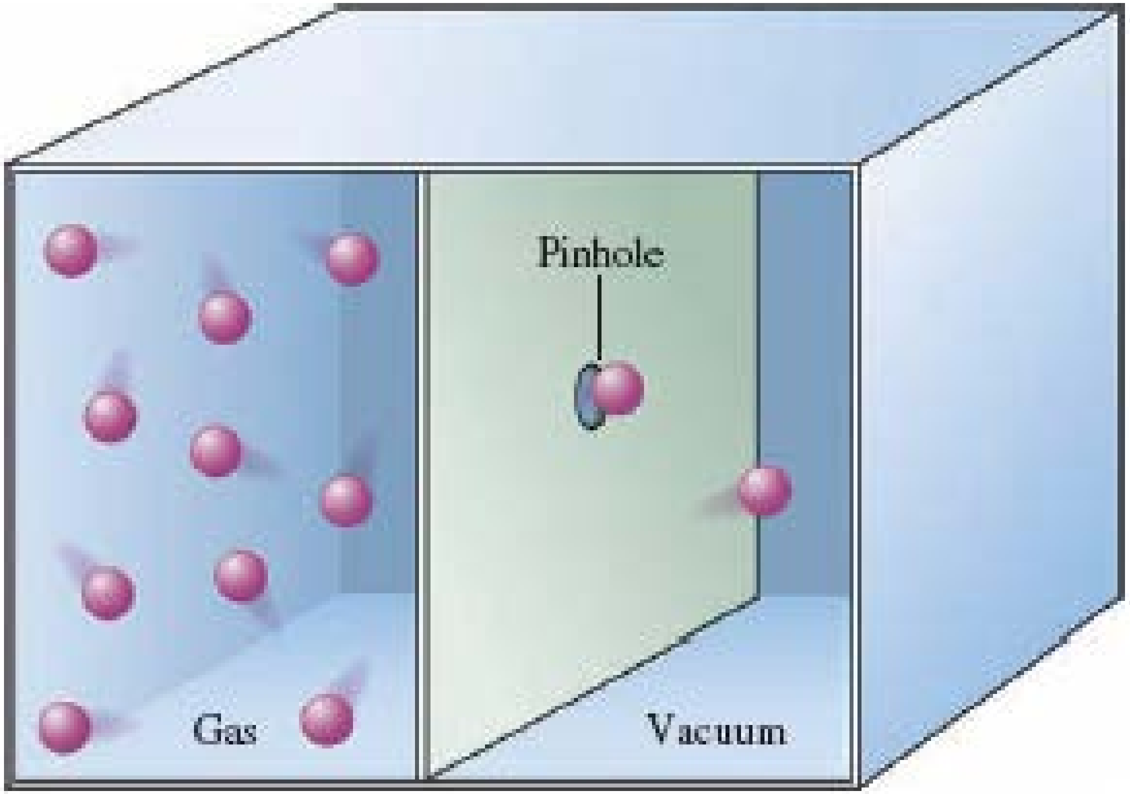
Diffusion

- A description for mixing gases.
- It also describes the movement of a gas from a region of high partial pressure to a region of lower partial pressure.
- When a small amount of ammonia is released at the front of a classroom, it takes some time before everyone in the room can smell it, because time is required for the ammonia to mix with air.
- The rate of diffusion is the rate of the mixing gases.

Effusion

is description for the passage of a gas through a tiny orifice into an evacuated chamber.

The rate of effusion measures the speed at which the gas is transferred into the chamber.



Effusion

- Thomas Graham (1805–1869), found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles.
- The relative rates of effusion of two gases at the same temperature and pressure are given by the inverse ratio of the square roots of the masses of the gas particles:

$$\boxed{\frac{\text{Rate of effusion for gas 1}}{\text{Rate of effusion for gas 2}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}}$$

Graham's law of effusion.

where M_1 and M_2 represent the molar masses of the gases.

Exercise

- Calculate the ratio of the effusion rates of hydrogen gas (H_2) and uranium hexafluoride (UF_6), a gas used in the enrichment process to produce fuel for nuclear reactors?

Solution

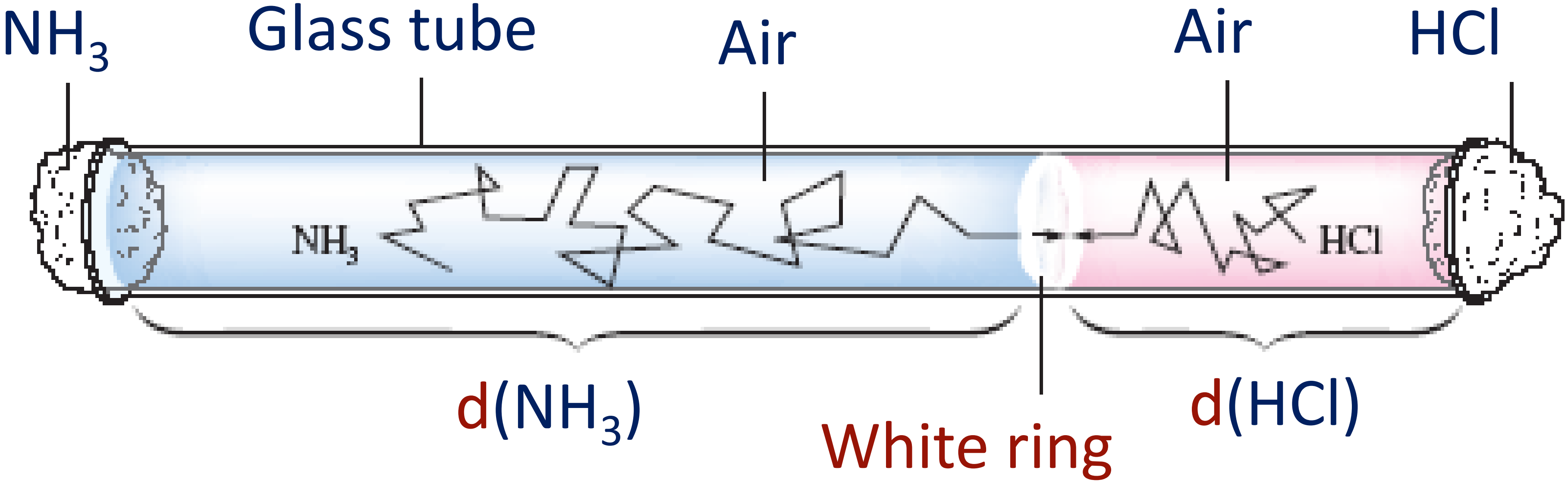
$$\frac{\text{Rate of effusion for } H_2}{\text{Rate of effusion for } UF_6} = \frac{\sqrt{M_{UF_6}}}{\sqrt{M_{H_2}}} = \frac{\sqrt{352.02}}{\sqrt{2.016}}$$

$$= 13.2$$

The effusion rate of H_2 is 13 times that of UF_6.

Experiment

- Two cotton plugs soaked in ammonia and hydrochloric acid are simultaneously placed at the ends of a long tube. A white ring is formed inside the tube but not immediately. Guess,
  - What is that white ring? Write the equation?
  - Where do you think will the white ring appear? Which side will it be closer to?
  - Why does it appear after certain time not immediately?



$$\mathrm{NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)}$$

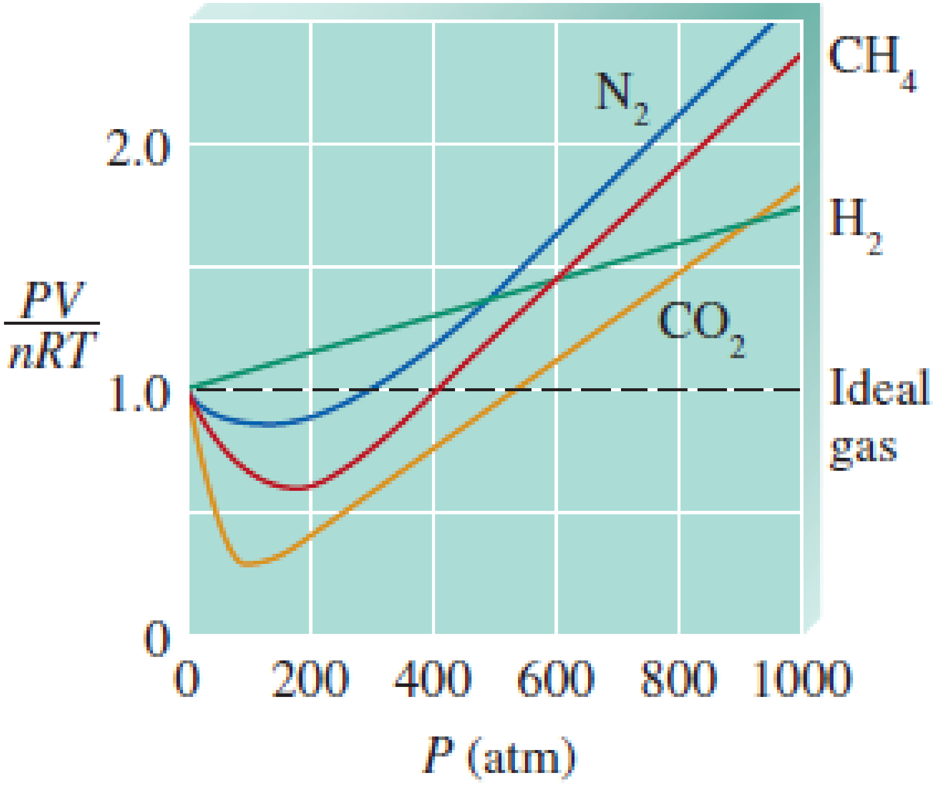
ammonium chloride

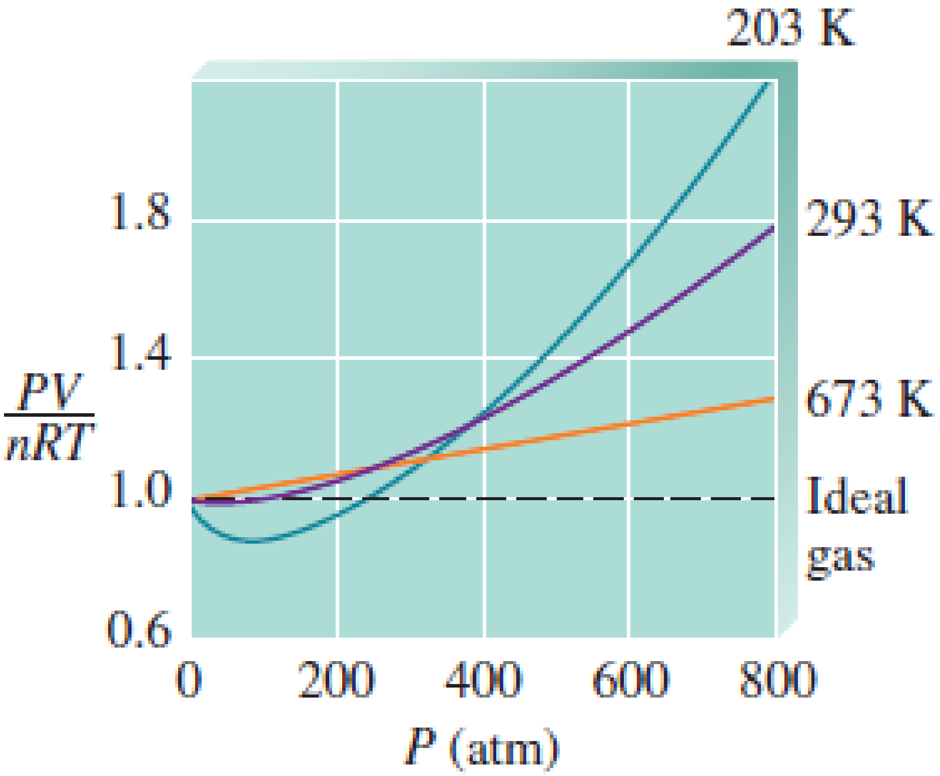
$$\boxed{\frac{\text{Distance traveled by NH}_3}{\text{Distance traveled by HCl}} = \frac{u_{rms(NH_3)}}{u_{rms(HCl)}} = \frac{\sqrt{M_{HCl}}}{\sqrt{M_{NH_3}}} = \frac{\sqrt{36.5}}{\sqrt{17}} = 1.5}$$

The tube contains air and thus the NH_3 and HCl molecules undergo many collisions with O_2 and N_2 molecules as they travel through the tube before reaction.

Real gases

- Almost all gases deviate from the ideal behavior, particularly at high pressure and low temperature.
- A real gas typically exhibits behavior that is closest to ideal behavior at low pressures and high temperatures.





Volume Correction

- KMT assumed a zero volume for the gas molecules under any condition.

!!!!!!!! <u>Wrong?</u>

- Instead of moving in V, molecules are moving in V-nb,

n: no of moles of a gas

b: (molar volume)

$$P = \frac{nRT}{V} \Rightarrow \boxed{P' = \frac{nRT}{V - nb}}$$

- HCl would have a slightly larger “b” than H_2

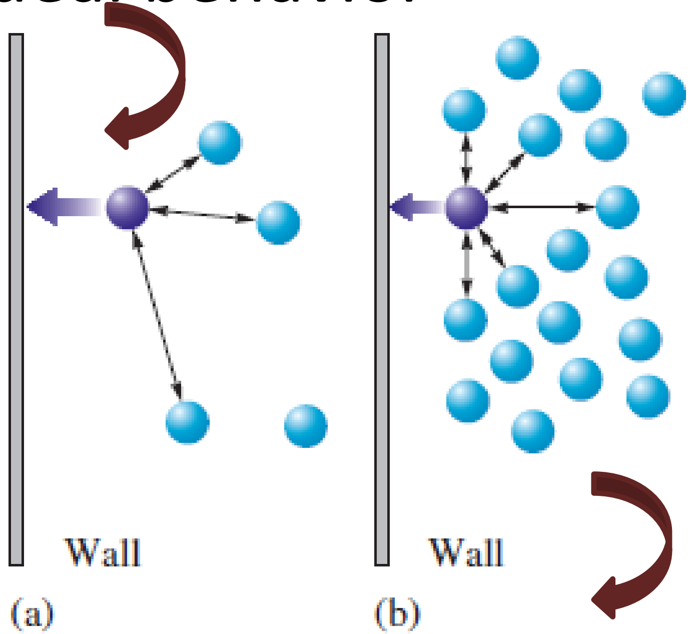
Pressure Correction

KMT assumed neither attraction nor repulsive forces (zero potential energy) between gas molecules under any condition

!!!!!!!! Wrong?

Observed pressure **P_{obs}** is smaller than it would be if the gas particles did not interact.

Low concentration
Low pressure
Ideal behavior



High concentration
High pressure
Real behavior

$$P_{obs} = P' - \text{ correction factor} = \frac{nRT}{V - nb} - \text{correction factor}$$

- Correction factor depends on the molar concentration$= \frac{n}{V}$

- The higher the concentration, the more likely a pair of gas particles will be close enough to attract each other.

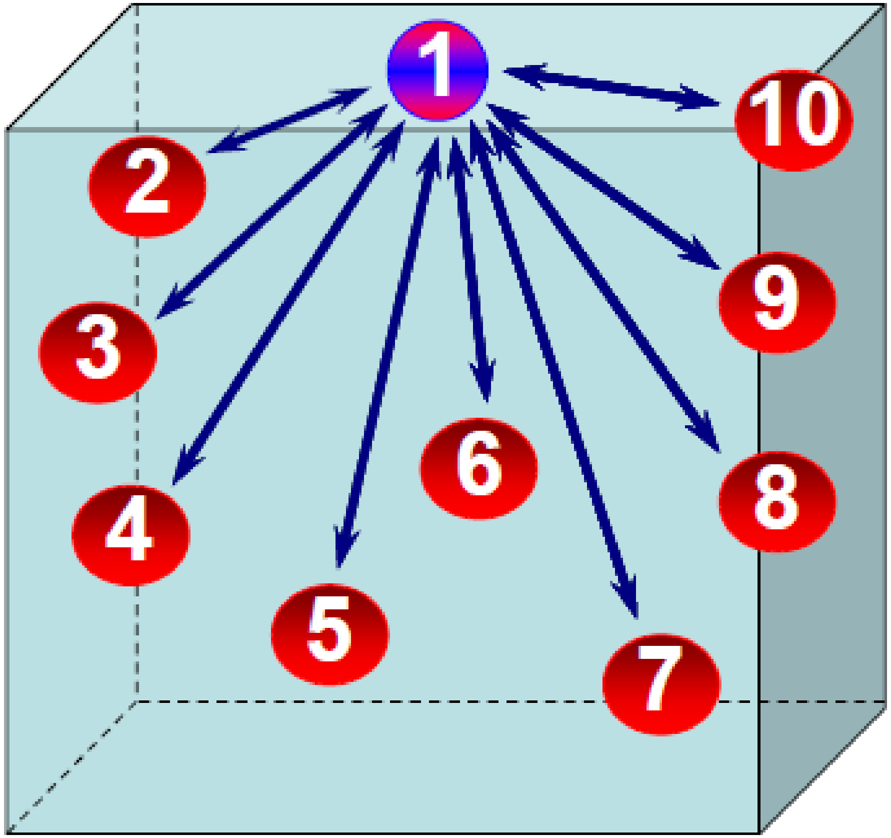
- For large numbers of particles, the number of interacting pairs of particles depends on the square of the number of particles and thus on the square of the concentration, or $\left(\frac{n}{V}\right)^2$.

- In a gas sample containing N particles, there is N – 1 partners available for each particle.

- For N particles, there are

$$\boxed{\frac{N(N-1)}{2}\,\text{pairs}}$$

$$\boxed{\frac{N(N-1)}{2} = \frac{10(10-1)}{2} = 45}$$



- For large N,

$$\boxed{\frac{N(N-1)}{2} \approx \frac{N^2}{2}}$$

Pressure correction factor $\propto$ (concentration)^2

Van der Waals Eqn.

$$P_{obs} = \frac{nRT}{V - nb} - a\left[\frac{n}{V}\right]^2$$

$$\boxed{\left[P_{obs} + \frac{an^2}{V^2}\right](V - nb) = nRT}$$

$\frac{V}{n}$ = molar volume

$a\left(\frac{n}{V}\right)^2$ = internal pressure of gas

$$a(HCl) > a(H_2)$$

HCl is a polar molecule and therefore has stronger intermolecular forces than H_2.

Van der Waals Eqn. vs. KMT

- Gases behave ideally at low pressures

❑ low $P \cong$ (large V), $\Rightarrow V >>> nb \Rightarrow \quad V - nb \approx V$

Ideal behavior

❑ high $P \cong$ small V, $\Rightarrow$ the volume of the particles becomes significant so that the volume available to the gas is significantly less than the container volume.

Real behavior

Van der Waals Eqn. vs. KMT

- Gases behave ideally at high temperatures.

☐ At high temperatures, the particles are moving so rapidly that the effects of interparticle interactions are not very important

Ideal behavior

Molar volume at STP

STP → 1 atm and $0^{O}C$

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

$$= \frac{(1.0\ \text{mol})\left(\frac{0.08206\ \text{L atm}}{\text{K mol}}\right)(273\ \text{K})}{1.0\ \text{atm}}$$

$$= 22.4\ \text{L}$$

Gas Stoichiometry

Exercise

Quicklime (CaO) is produced by the thermal decomposition of calcium carbonate ($CaCO_3$). Calculate the volume of CO_2 at STP produced from the decomposition of 152 g $CaCO_3$ by the reaction.

Solution

$$\mathrm{CaCO_3(s) \rightarrow CaO(s) + CO_2(g)}$$

- Calculate the moles of CaCO3 (100.9 g/mol)

$$152\ \mathrm{g\ CaCO_3} \times \frac{1\ \mathrm{mol\ CaCO_3}}{100.09\ \mathrm{g\ CaCO_3}} = 1.52\ \mathrm{mol\ CaCO_3}$$

- The mole ratio between CO_2 and $CaCO_3$ in the balanced equation is 1:1.
- Hence, 1.52 moles of CO_2 will be produced.
- Convert from moles to volume

$$\boxed{1.52\ \text{mol CO}_2 \times \frac{22.4\ \text{L CO}_2}{1\ \text{mol CO}_2} = 34.1\ \text{L CO}_2}$$

Homework

A sample of methane gas having a volume of 2.80 L at 25°C and 1.65 atm was mixed with a sample of oxygen gas having a volume of 35.0 L at 31°C and 1.25 atm. The mixture was then ignited to form carbon dioxide and water. Calculate the volume of CO_2 formed at a pressure of 2.50 atm and a temperature of 125°C. (Hint: think about the limiting reactant)

Molar Mass of a Gas/Gas density

$$\mathrm{n} = \frac{\text{mass (g)}}{\text{molar mass (g/mol)}} = \frac{\mathrm{m}}{\mathrm{M}}$$

$$\boxed{P = \frac{nRT}{V} = \frac{\left(\frac{m}{M}\right)RT}{V} = \left(\frac{m}{V}\right)\left(\frac{RT}{M}\right) = \frac{dRT}{M}}$$

$$M = \frac{dRT}{P}$$

Exercise

- The density of a gas was measured at 1.50 atm and 27°C and found to be 1.95 g/L. Calculate the molar mass of the gas?

Solution

$$M = \frac{dRT}{P}$$

$$= \frac{\left(1.95\,\frac{\mathrm{g}}{\mathrm{L}}\right)\left(\frac{0.08206\ \mathrm{L\ atm}}{\mathrm{K\ mol}}\right)(300\ \mathrm{K})}{1.0\ \mathrm{atm}}$$

$$= 32.0\ \frac{\mathrm{g}}{\mathrm{mol}}$$

Collecting a gas over water

- A mixture of gases results whenever a gas is collected by displacement of water.
- e.g., O_2 production by thermal decomposition of $KClO_3$. (MnO_2 is mixed with the $KClO_3$ to make the reaction faster).

Henry's law

- The concentration of a gas in a solution, (S_g) is proportional to the partial pressure of this gas over the solution

$$S_g = k\,P_g$$

When P increases, the rate at which the gas molecules enter the solution increases and hence, the equilibrium concentration of the gas in solution increases

Exercise

- A sample of solid potassium chlorate ($KClO_3$) was heated and decomposed. The oxygen produced was collected by displacement of water at 22°C at a total pressure of 754 torr. The volume of the gas collected was 0.650 L, and the vapor pressure of water at 22°C is 21 torr. Calculate the partial pressure of O_2 in the gas collected and the mass of $KClO_3$ in the sample that was decomposed?

Solution

$$2\mathrm{KClO_3(s)} \rightarrow 2\mathrm{KCl(s)} + 3\mathrm{O_2(g)}$$

$$P_T = P_{O_2} + P_{H_2O} = P_{O_2} + 21\ \text{torr} = 754\ \text{torr}$$

Calc P_{O_2}

$$\boxed{P_{O_2} = P_T - P_{H_2O} = 754\ \text{torr} - 21\ \text{torr} = 733\ \text{torr}}$$

$$P_{O_2} = 733\ \text{torr} \times \frac{1\ \text{atm}}{760\ \text{torr}} = 0.964\ \text{atm}$$

Calc n_{O_2}

$$n_{O_2} = \frac{(0.964\ \text{atm})\ (0.650\text{L})}{\left(\frac{0.08206\ \ \text{L atm}}{\text{K}\ \ \text{mol}}\right)\ (295\ \text{K})} = 2.59 \times 10^{-2}\text{mol}$$

Required moles of $KClO_3$

$$2.59 \times 10^{-2}\ \mathrm{mol\ O_2} \times \frac{2\ \mathrm{mol\ KClO_3}}{3\ \mathrm{mol\ O_2}}$$

$$= 1.73 \times 10^{-2}\ \mathrm{mol\ KClO_3}$$

$KClO_3$ (molar mass = 122.6 g/mol)

Mass of $KClO_3$

$$\boxed{1.73 \times 10^{-2}\ \mathrm{mol\ KClO_3} \times \frac{122.6\ \mathrm{g\ KClO_3}}{1\ \mathrm{mol\ KClO_3}} = \mathbf{2.12\ g}}$$

Exercise

- Nitrogen trichloride gas reacts with water to form ammonia and hypochlorous acid, HOCl (aq), the main component in household bleach.
  a. Write a balanced equation for this reaction.
  b. How many moles of NH_3 are produced from 275 mL water (d = 1 g/mL) and excess NCl_3?
  c. What mass of NCl_3 is required to produce 100 g ammonia?
  d. Suppose 58 g NCl_3 and 15 g water were reacted. Which is the limiting reagent? What is the theoretical yield of ammonia and HOCl? (in moles and grams)
  e. above: If the yield of NH_3 were only 4.4 g, what is the percent yield?

Solution

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$

Excess NCl_3 $\Rightarrow$ it is not limiting.

$$\text{Mass of water} = \text{density}\left(\frac{1\text{ g}}{\text{mL}}\right) \times \text{Volume }(275\text{ mL}) = 275\text{ g}$$

$$\text{No. of moles of water} = \frac{\text{mass }(275\text{ g})}{\text{molar mass}(18\text{ g/mol})} = 15.3\text{ mol}$$

Stoichiometry: $3H_2O : NH_3$

$$\boxed{\text{No. of moles of } NH_3 = 15.3 \times \frac{1}{3} = 5.1\text{ mol}}$$

To produce 100 g NH_3

Assuming NCl_3 is limiting

No. of moles of NH_3

$$= \frac{mass\ (100\ g)}{molar\ mass\ (14 + 3\ (1) = 17\ g/mol)} = 5.88\ \text{mol}$$

Stoichiometry: $NCl_3 : NH_3$

$$\text{No. of moles of } NCl_3 = 5.88 \times \frac{1}{1} = 5.88\ \text{mol}$$

Mass of NCl_3

$$= \text{No. of moles } (5.88\ \cancel{\text{mol}}) \times \text{molar mass } \left(\frac{120.5\text{g}}{\cancel{\text{mol}}}\right)$$

$$= 708.54\ \text{g}$$

58 g NCl_3 and **15 g** water were reacted. limiting reagent? theoretical yield?

$$NCl_3 + 3H_2O \rightarrow NH_3 + 3HOCl$$

Stoichiometry	**1**	**3**	**1**	**3**
Masses, g	58	15	??	??
Reacted moles	0.48	0.83		
Ratio	$\frac{o.48}{1} = 0.48$	$\frac{o.83}{3} = 0.28$		
Limiting Reactant		√√√		
Reacted moles	0.28	0.83	0.28	0.83
Th. Yield, g			4.7	43.6

$$\text{Percent Yield of } NH_3 = \frac{4.4}{4.7} \times 100 = 93.6\ \%$$

Homework

- Phosphorus is made from reacting calcium phosphate with both silicon dioxide and elemental carbon to produce elemental phosphorus, P_4, carbon monoxide and calcium silicate, $CaSiO_3$.
  a. Write the overall balanced reaction ?
  b. Suppose that 500.0 g calcium phosphate reacted with 300.0 g silicon dioxide and 100.0 g carbon. Determine the limiting reagent?
  c. What mass of phosphorus is theoretically expected to be produced?
  d. Suppose that the process is known to be typically 70% efficient. What mass of phosphorus can we realistically expect to get?

Exercise

- Using the van der Waals equation, calculate the pressures exerted by 1.00 mole of Ar gas in a 22.4 L container at 273 K. How much is the pressure deviation from ideal behavior? Which is most likely behind the deviation from ideal behavior: the volumes of the molecules or intermolecular attractions? The van der Waals constants for Ar are listed below:

Substance	a (L^2.atm mol^{-2})	b (L mol^{-1})
Ar	1.337	3.2

Solution

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

$$P = \frac{(1\ \text{mol})(0.0821\ \text{L atm mol}^{-1}\text{K}^{-1})(273\text{K})}{22.4\text{L} - [(1\ \text{mol}).(\ 3.2\text{Lmol}^{-1})]} - 1.337\left[\frac{1\ \text{mol}}{22.4}\right]^2$$

P= 1.1674–0.00266 = 1.1648 atm

If behaved ideally (PV=nRT), P=1 atm

- In the real case, the second value, 0.00266 atm is very small, which indicates that the main reason for the tiny deviation from ideal behavior is due to the volumes of the molecules rather than intermolecular attractions.
- This makes sense for Ar that has only very weak **London dispersion forces**