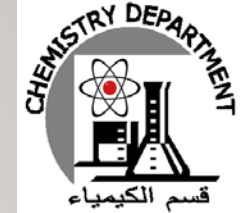




# General Chemistry II

## Chem 102

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### Lecture 3

# Ideal & Real Gases

Ahmad Alakraa

# The Ideal Gas Law

*Boyle's law:*  $V = \frac{k}{P}$  (constant  $T, n$ )

*Charles's law:*  $V = bT$  (constant  $P, n$ )

*Avogadro's law:*  $V = an$  (constant  $T, P$ )

$$V = R \left( \frac{Tn}{P} \right)$$

$$PV = nRT$$

**Equation of  
state for gases**

**R** : Universal gas constant  $R = \frac{0.08206 \text{ L atm}}{\text{K mol}}$

This equation is mostly obeyed at **low pressures** and **high temperatures**

# Universal Gas Constant

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.414 \text{ L}}{1 \text{ mol} \times 273.15 \text{ K}} =$$

$$0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$= 82 \text{ mL atm K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$= 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$$

# 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”

$$\begin{aligned}P_{\text{Total}} &= P_1 + P_2 + P_3 + \dots \\ &= \frac{n_1 RT}{V} + \frac{n_2 RT}{V} + \frac{n_3 RT}{V} + \dots \\ &= (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = \frac{n_{\text{Total}} RT}{V}\end{aligned}$$

- 🍷 **P** is not affected 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 prevent “the bends.” For a particular dive, 46 L He at 25°C and 1.0 atm and 12 L O<sub>2</sub> 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

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

$$n_{\text{O}_2} = \frac{(1.0 \text{ atm})(12 \text{ L})}{(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})} = 0.49 \text{ mol}$$

**Calculate** the partial pressure for each gas in the tank

$$P_{He} = \frac{(1.9 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})}{(5 \text{ L})}$$
$$= 9.3 \text{ atm}$$

$$P_{O_2} = \frac{(0.49 \text{ mol})(0.08206 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(298 \text{ K})}{(5 \text{ L})}$$
$$= 2.4 \text{ atm}$$

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

# Mole fraction, $\chi$

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

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

$$= \frac{(V/RT)P_1}{(V/RT)(P_1 + P_2 + P_3 + \dots)}$$

# Mole fraction, $\chi$

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

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

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

$$\sum_i \chi_i = 1$$

## 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<sub>2</sub> present at 25°C?

## Solution

$$\chi_{O_2} = \frac{P_{O_2}}{P_T} = \frac{156 \text{ torr}}{743 \text{ torr}} = 0.210$$

# Homework

A rigid 9.50 L flask contained a mixture of 3.00 moles of hydrogen (H<sub>2</sub>) gas, 1.00 moles of oxygen (O<sub>2</sub>) 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<sup>-1</sup>) 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.



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

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

## 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

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

## 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.

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

## 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.

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

# 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.

# Root Mean Square Velocity

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

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

$$(KE)_{\text{avg}} = N_A \left( \frac{1}{2} m \overline{u^2} \right)$$

$N_A m = M$       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”  $u_{\text{rms}}$ :

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

$$(\text{KE})_{\text{avg}} = \frac{3}{2} RT = N_A \left( \frac{1}{2} m \overline{u^2} \right)$$

$$N_A m = M$$

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

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$

$$R = 8.3145 \text{ J/K.mol}$$

✚ For a large number of particles ( $n$  in mol) moving in random directions: →

→ 
$$PV = \frac{1}{3} n N_A \overline{m u^2} = \frac{2}{3} n N_A \left( \frac{1}{2} \overline{m u^2} \right)$$

✚ However

$$(KE)_{avg} = N_A \left( \frac{1}{2} \overline{m u^2} \right)$$

→ 
$$PV = \frac{2}{3} n (KE)_{avg}$$

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

As →

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

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

$$(\text{KE})_{\text{avg}} = \frac{3}{2} RT$$

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

## The Kelvin Temperature

is an index of the random motions of the gas particles

$$PV = \frac{1}{3} n N_A m \overline{u^2}$$

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



$$\overline{u^2} = \frac{3RT}{N_A m}$$

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

## Exercise

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

## Solution

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

$$\begin{aligned} u_{\text{rms}} &= \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \left( \frac{8.314 \text{ J}}{\text{K mol}} \right) (298 \text{ K})}{\left( 4.0 \times 10^{-3} \frac{\text{kg}}{\text{mol}} \right)}} \\ &= \sqrt{1.86 \times 10^6 \frac{\text{J}}{\text{kg}}} = \sqrt{1.86 \times 10^6 \frac{\text{kg m}^2}{\text{kg s}^2}} \\ &= \frac{1.36 \times 10^3 \text{ m}}{\text{s}} \end{aligned}$$

## Exercise

■ At the same temperature, compare  $U_{\text{rms}} \text{H}_2$  with  $U_{\text{rms}} \text{O}_2$

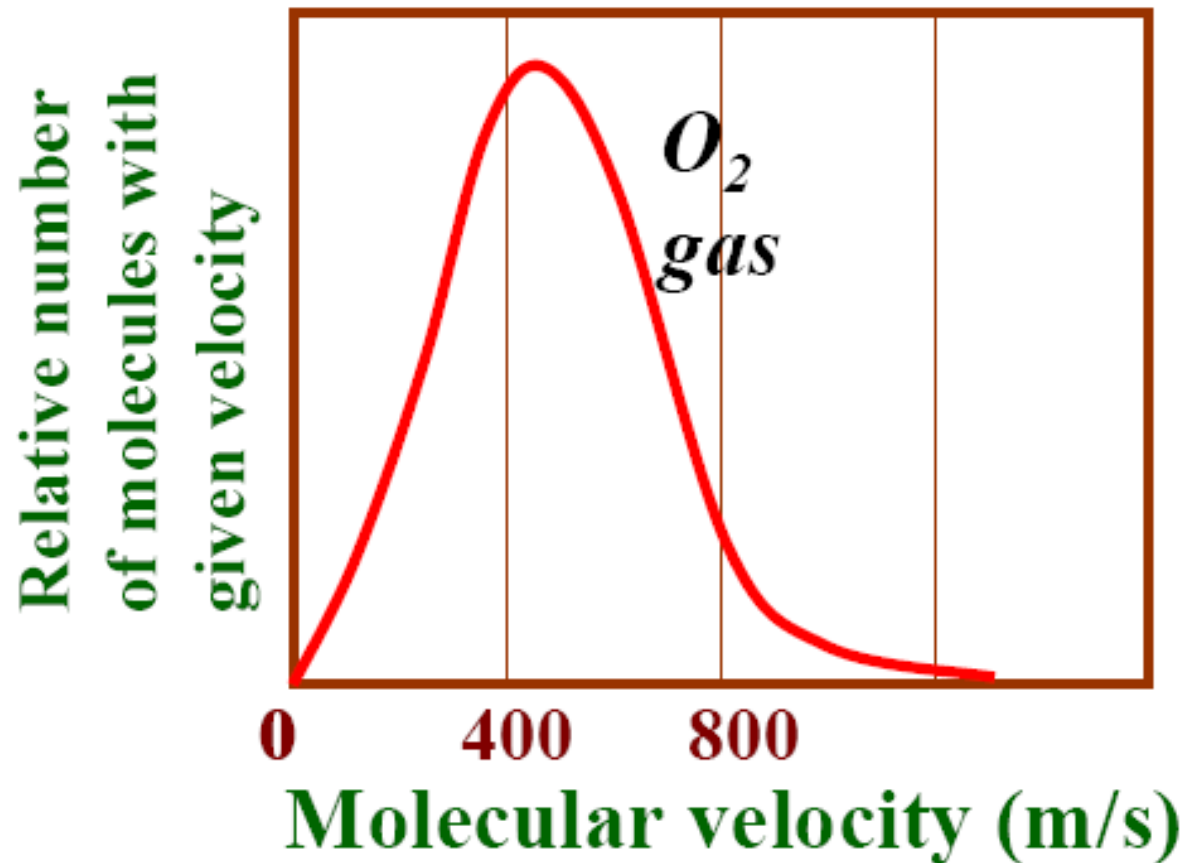
## Solution

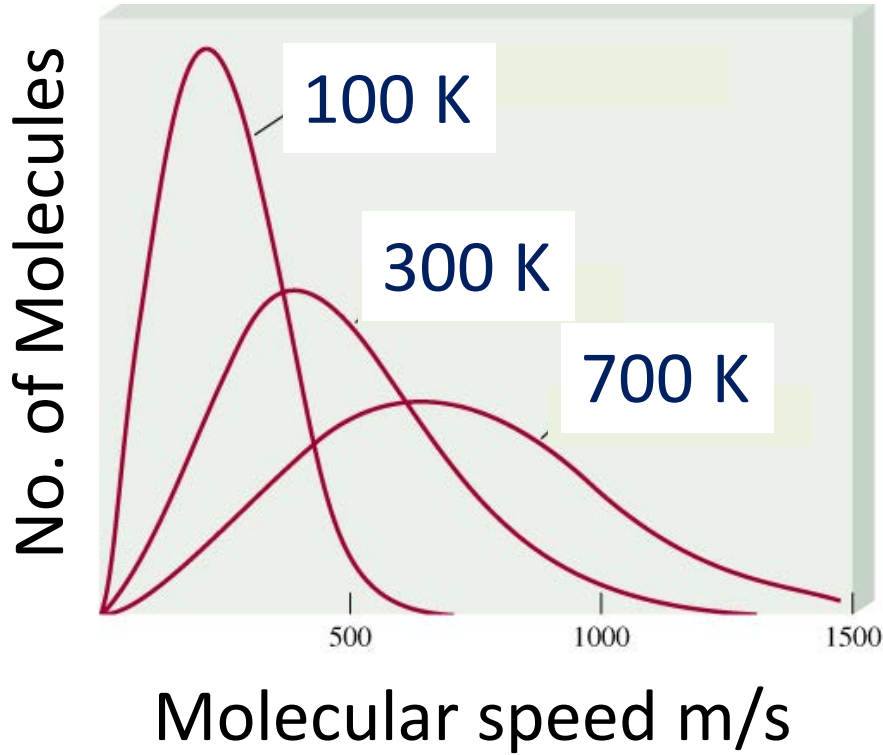
$$\frac{u_{\text{rms}}(\text{H}_2)}{u_{\text{rms}}(\text{O}_2)} = \frac{\sqrt{\frac{3RT}{M_{\text{H}_2}}}}{\sqrt{\frac{3RT}{M_{\text{O}_2}}}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{H}_2}}} = \sqrt{\frac{32}{2}} = 4$$

Hydrogen moves 4 times faster than oxygen

# Mean free Path

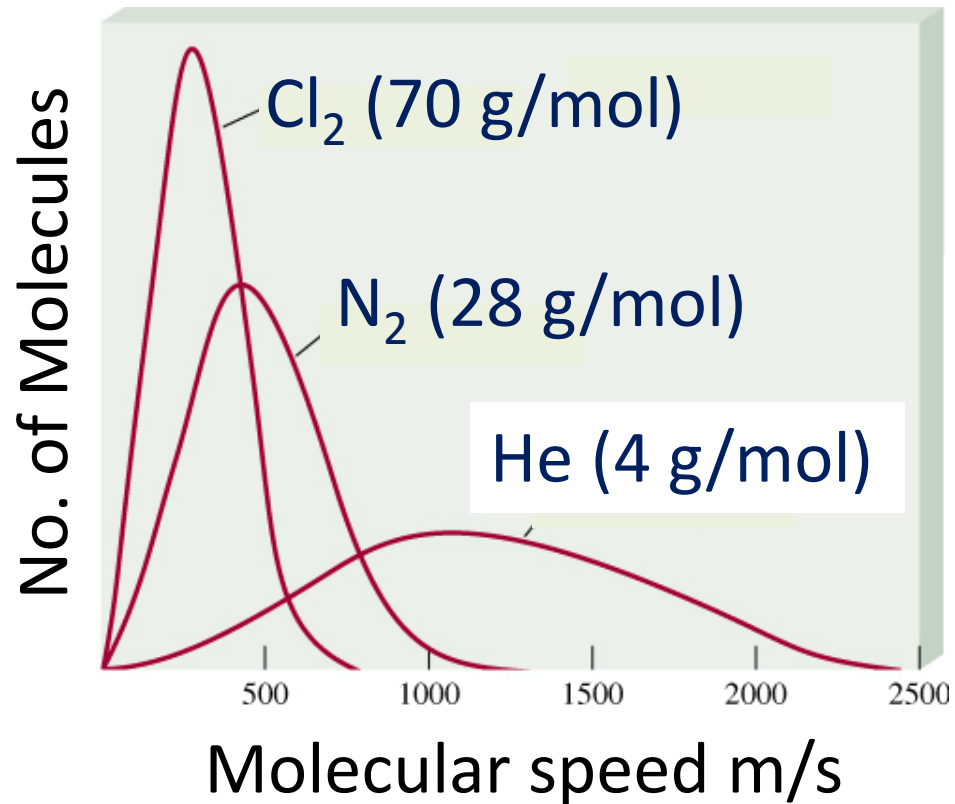
It is the average distance a particle travels between collisions in a particular gas sample.





The distribution of speeds for  $N_2$  gas (28 g/mol) molecules at three different temperatures (100, 300 & 700 K)

The distribution of speeds of 3 gases ( $Cl_2=70$ ), ( $N_2=28$ ), & ( $H=4$ ) at same  $T=300$  K



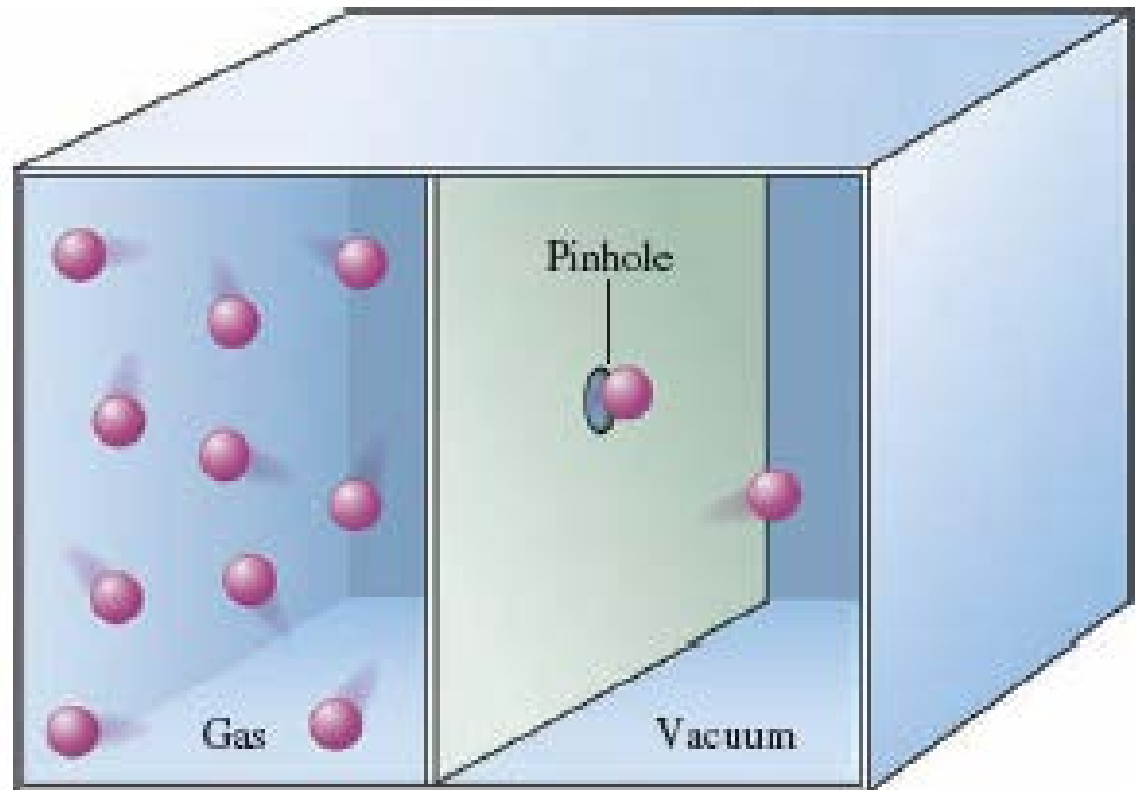
# Diffusion

- 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:

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

**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  $UF_6$ .

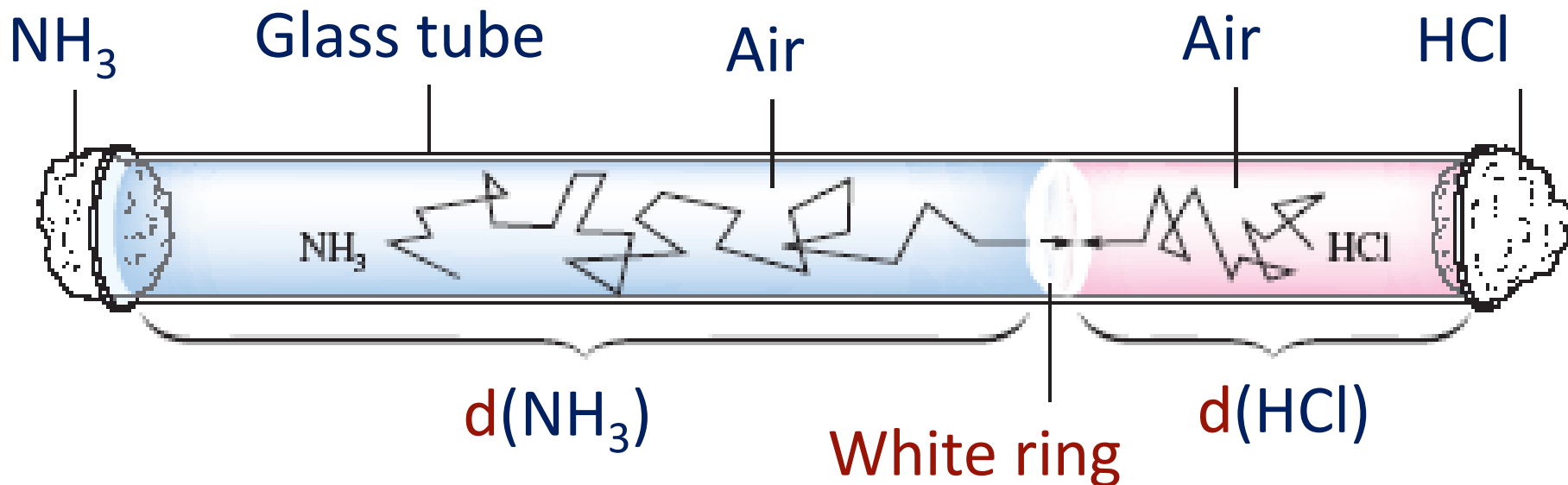
# Experiment

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?



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

The tube contains **air** and thus the **NH<sub>3</sub>** and **HCl** molecules undergo many collisions with **O<sub>2</sub>** and **N<sub>2</sub>** molecules as they travel through the tube before reaction.

# Molar volume at STP

STP  1 atm and 0°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<sub>3</sub>). Calculate the volume of CO<sub>2</sub> at STP produced from the decomposition of 152 g CaCO<sub>3</sub> by the reaction.

## Solution



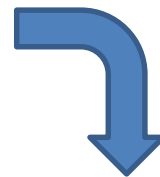
✚ Calculate the moles of CaCO<sub>3</sub> (100.9 g/mol)

$$152 \text{ g CaCO}_3 \times \frac{1 \text{ mol CaCO}_3}{100.09 \text{ g CaCO}_3} = 1.52 \text{ mol CaCO}_3$$

✚ The mole ratio between  $\text{CO}_2$  and  $\text{CaCO}_3$  in the balanced equation is 1:1.

✚ Hence, 1.52 moles of  $\text{CO}_2$  will be produced.

✚ Convert from moles to volume



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

# 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<sub>2</sub> 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

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

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

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

## 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

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

$$\begin{aligned} &= \frac{\left(1.95 \frac{\text{g}}{\text{L}}\right) \left(\frac{0.08206 \text{ L atm}}{\text{K mol}}\right) (300 \text{ K})}{1.0 \text{ atm}} \\ &= 32.0 \frac{\text{g}}{\text{mol}} \end{aligned}$$

# 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 ( $\text{KClO}_3$ ) was heated and decomposed. The oxygen produced was collected by displacement of water at  $22^\circ\text{C}$  at a total pressure of 754 torr. The volume of the gas collected was 0.650 L, and the vapor pressure of water at  $22^\circ\text{C}$  is 21 torr. Calculate the partial pressure of  $\text{O}_2$  in the gas collected and the mass of  $\text{KClO}_3$  in the sample that was decomposed?

## Solution



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

↪ **Calc  $P_{O_2}$**

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

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

↪ **Calc  $n_{O_2}$**

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

## Required moles of $\text{KClO}_3$

$$2.59 \times 10^{-2} \text{ mol O}_2 \times \frac{2 \text{ mol KClO}_3}{3 \text{ mol O}_2} = 1.73 \times 10^{-2} \text{ mol KClO}_3$$

$\text{KClO}_3$  (molar mass = 122.6 g/mol)

## Mass of $\text{KClO}_3$

$$1.73 \times 10^{-2} \text{ mol KClO}_3 \times \frac{122.6 \text{ g KClO}_3}{1 \text{ mol KClO}_3} = 2.12 \text{ g}$$

# Exercise

- Nitrogen trichloride gas reacts with water to form ammonia and hypochlorous acid, HOCl (aq), the main component in household bleach.
- Write a balanced equation for this reaction.
  - How many moles of  $\text{NH}_3$  are produced from 275 mL water ( $d = 1 \text{ g/mL}$ ) and excess  $\text{NCl}_3$ ?
  - What mass of  $\text{NCl}_3$  is required to produce 100 g ammonia?
  - Suppose 58 g  $\text{NCl}_3$  and 15 g water were reacted. Which is the limiting reagent? What is the theoretical yield of ammonia and HOCl? (in moles and grams)
  - above: If the yield of  $\text{NH}_3$  were only 4.4 g, what is the percent yield?

## **Solution**



**Excess  $\text{NCl}_3$**   $\Rightarrow$  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:**  $3\text{H}_2\text{O} : \text{NH}_3$

$$\text{No. of moles of } \text{NH}_3 = 15.3 \times \frac{1}{3} = 5.1 \text{ mol}$$

To produce 100 g  $\text{NH}_3$

Assuming  $\text{NCl}_3$  is limiting

$$\begin{aligned} &\text{No. of moles of } \text{NH}_3 \\ &= \frac{\text{mass (100 g)}}{\text{molar mass (14 + 3 (1) = 17 g/mol)}} = 5.88 \text{ mol} \end{aligned}$$

↪ **Stoichiometry:**  $\text{NCl}_3 : \text{NH}_3$

$$\text{No. of moles of } \text{NCl}_3 = 5.88 \times \frac{1}{1} = 5.88 \text{ mol}$$

Mass of  $\text{NCl}_3$

$$\begin{aligned} &= \text{No. of moles (5.88 mol)} \times \text{molar mass } \left( \frac{120.5 \text{ g}}{\text{mol}} \right) \\ &= 708.54 \text{ g} \end{aligned}$$

58 g  $\text{NCl}_3$  and 15 g water were reacted. limiting reagent?  
theoretical yield?



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

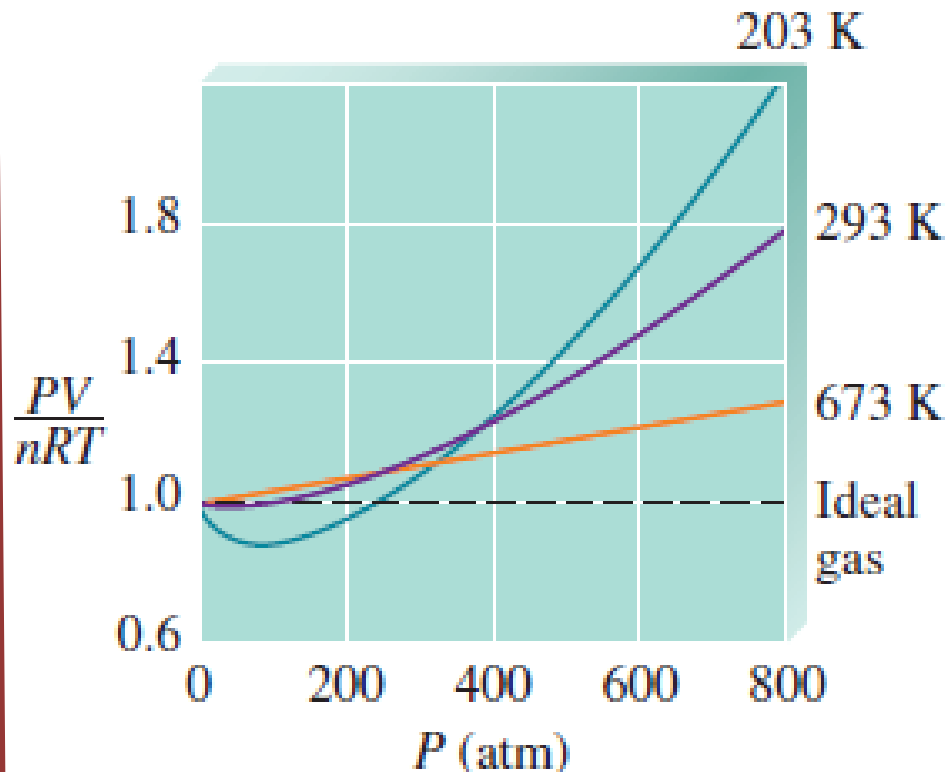
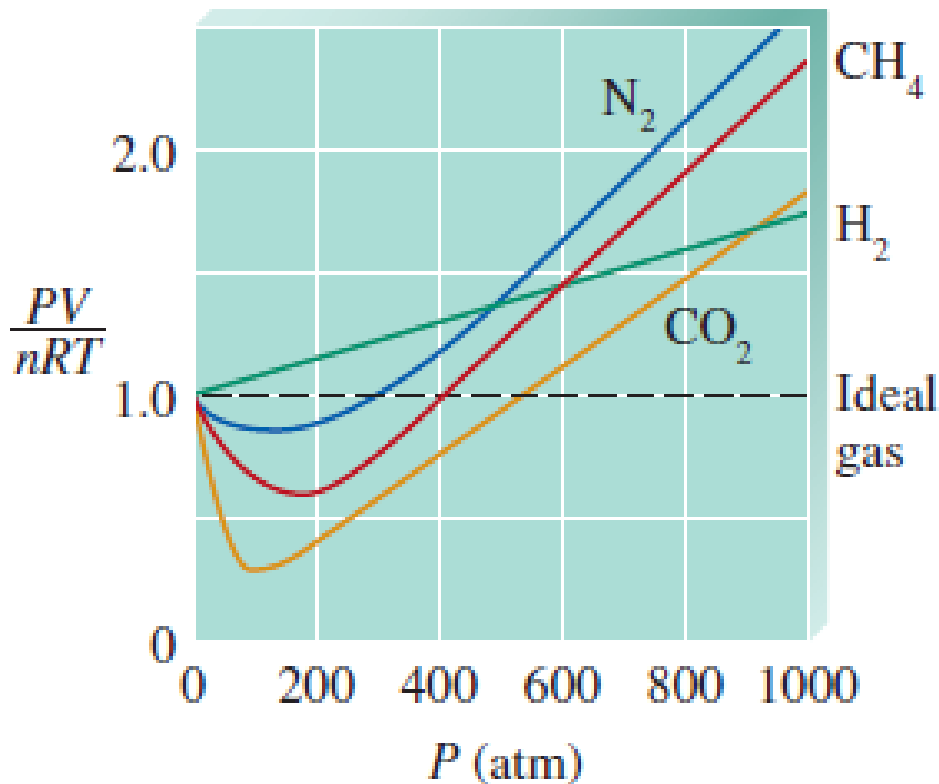
$$\text{Percent Yield of } \text{NH}_3 = \frac{4.4}{4.7} \times 100 = 93.6 \%$$

# 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?

# Real gases

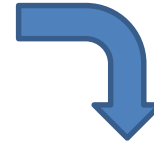
- Almost all gases deviate from the ideal behavior, particularly at high pressure and low temperature.
- A real gas typically exhibits behavior that is closest to ideal behavior at low pressures and high temperatures.



# Volume Correction

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

!!!!!!! Wrong?

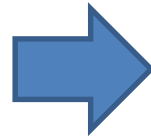


◆ Instead of moving in **V**, molecules are moving in **V-nb**,

**n**: no of moles of a gas

**b**: (molar volume)

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



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

◆ **HCl** would have a slightly larger “**b**” than **H<sub>2</sub>**

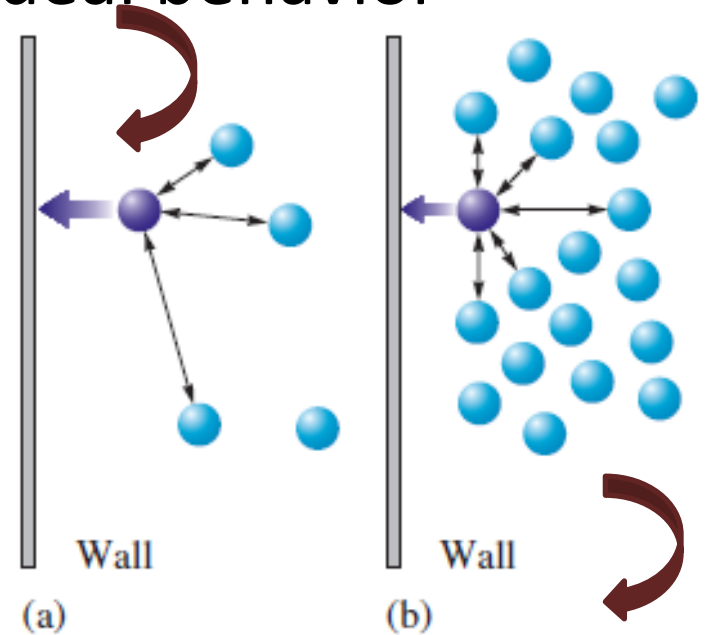
# Pressure Correction

**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.

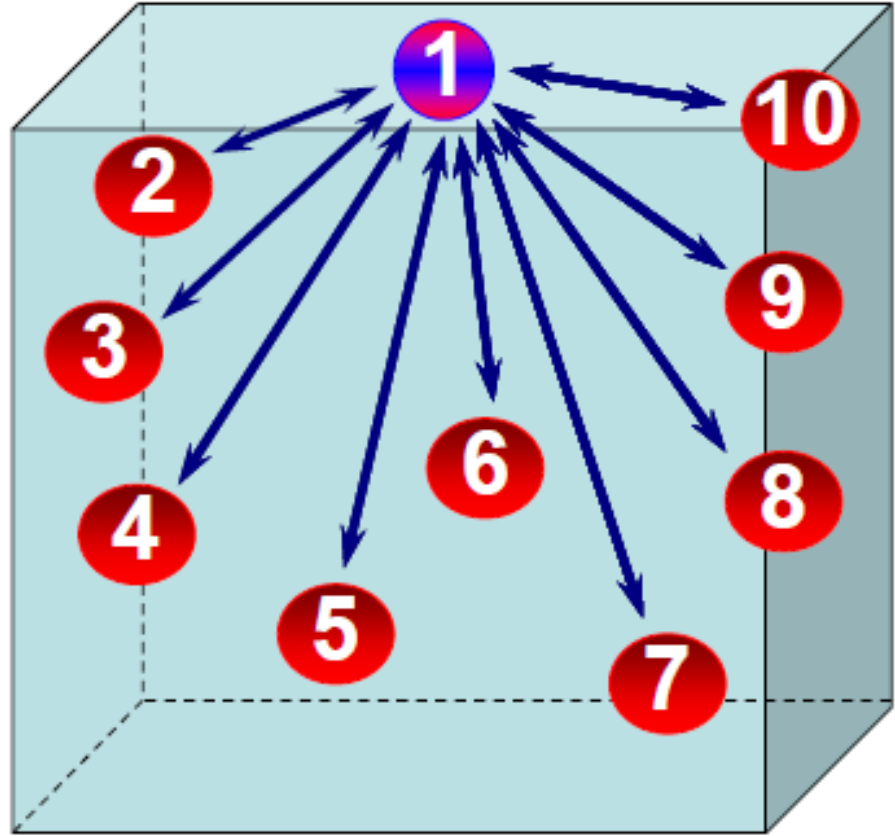
For N particles, there are

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

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

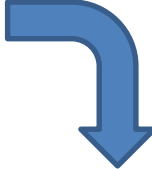
For large N,

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



**Pressure correction factor**  $\propto$  (concentration)<sup>2</sup>

# Van der Waals Eqn.

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


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

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

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

$$a(\text{HCl}) > a(\text{H}_2)$$

HCl is a **polar** molecule and therefore has **stronger** intermolecular forces than H<sub>2</sub>.

# Van der Waals Eqn. vs. KMT

✚ Gases behave ideally at low pressures

$$\square \text{ low } P \cong (\text{large } V), \quad \Rightarrow V \gg \gg nb \Rightarrow V - nb \approx V$$



**Ideal behavior**

$\square$  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**

# 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 <sup>2</sup> .atm mol <sup>-2</sup> )	b (L mol <sup>-1</sup> )
Ar	1.337	3.2

## Solution

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

P

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

$$P = 1.1674 - 0.00266 = 1.1648 \text{ atm}$$

If behaved ideally ( $PV=nRT$ ),  $P=1 \text{ atm}$

- ◆ 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**