Chapter 5

Gases

Properties of Gases

- Occupy the entire volume of their container
- Compressible
- Flow readily and mix easily
- Have low densities, low molecular weight

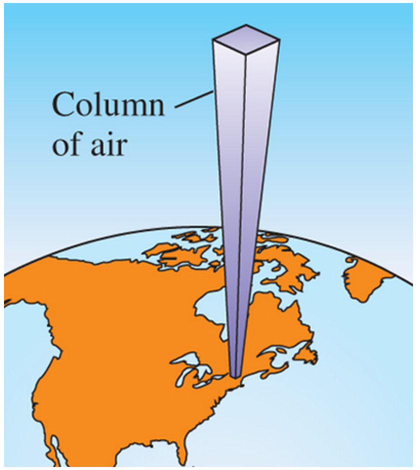
Some common gases:

Elements	Compounds
H_2 (molecular hydrogen)	HF (hydrogen fluoride)
N_2 (molecular nitrogen)	HCl (hydrogen chloride)
O_2 (molecular oxygen)	HBr (hydrogen bromide)
O_3 (ozone)	HI (hydrogen iodide)
F_2 (molecular fluorine)	CO (carbon monoxide)
Cl_2 (molecular chlorine)	CO_2 (carbon dioxide)
He (helium)	NH_3 (ammonia)
Ne (neon)	NO (nitric oxide)
Ar (argon)	NO_2 (nitrogen dioxide)
Kr (krypton)	N_2O (nitrous oxide)
Xe (xenon)	SO_2 (sulfur dioxide)
Rn (radon)	H_2S (hydrogen sulfide)

Atmospheric Pressure

$$\text{Pressure} = \frac{\text{Force (N)}}{\text{Area (m}^2\text{)}}$$

Force = mass x acceleration
= kg x m/s^2

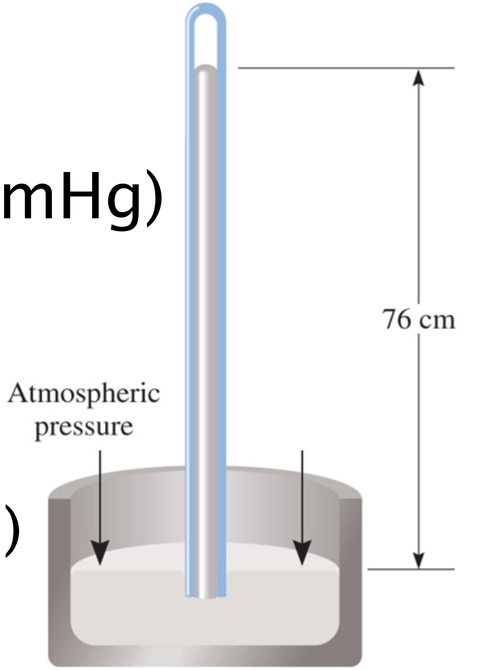


Atmospheric pressure

- Pressure from earth's atmosphere at sea level
- Equal to 1 atmosphere (atm)

Barometer

- Used to measure atmospheric pressure
- Measures height of Hg column in mm (mmHg)
- At sea level height is exactly 760mm



In other pressure units: 1atm is equal to.....

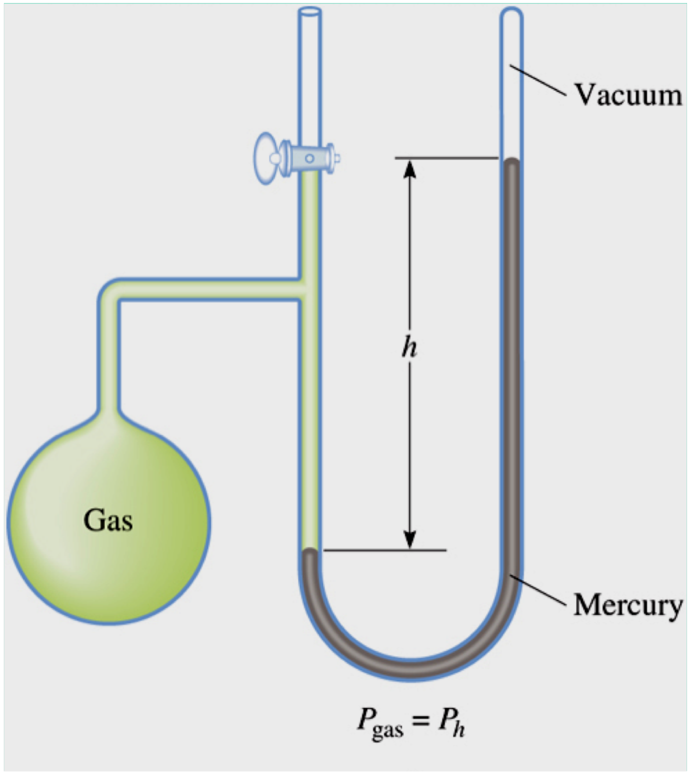
760 mmHg	760 torr	101325 Pa (N/m^2)
101.325 kPa	29.921 in. Hg	14.695 948 psi

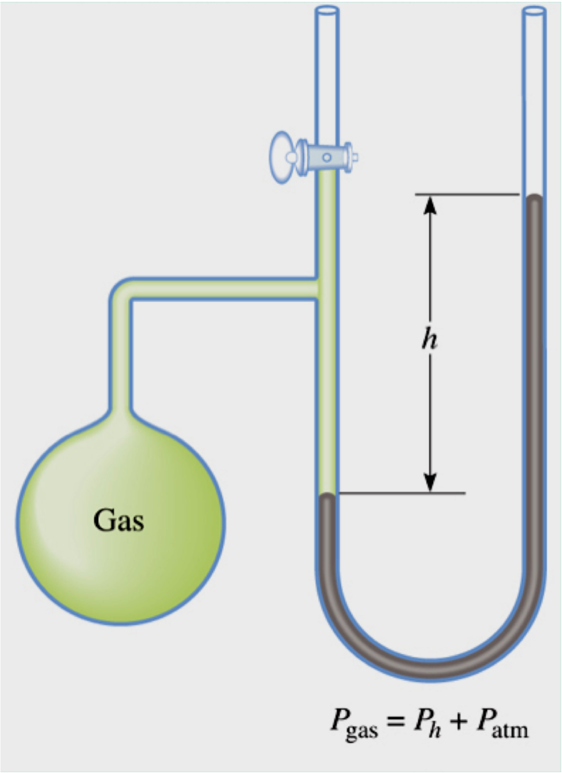
Measuring Experimental Gas Pressure

A manometer measures pressure of gases

Closed tube manometer
Best for pressures <1atm
P_{gas} = Height = mm Hg

Open tube manometer
Best for pressures ≥1atm
P_{gas} = 760mm Hg + height





Use for Changing Conditions
(have initial & final)

$$\frac{P_1 V_1}{n_1 T_1} = \frac{P_2 V_2}{n_2 T_2}$$

Use for Constant Conditions

$$\mathbf{PV = nRT}$$

Gas Laws

In case you should need them for HW:

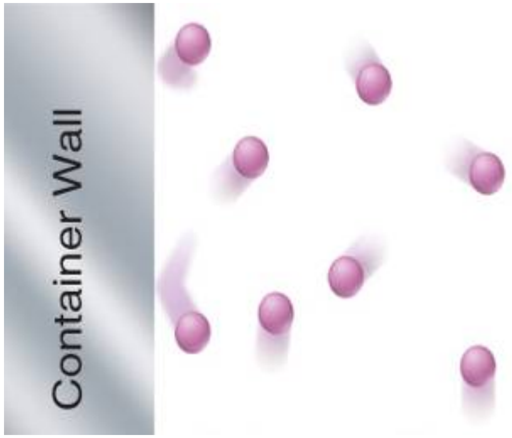
°C = (°F – 32) x 5 / 9

°F = (°C x 9 / 5) + 32

Kinetic Molecular Theory

Based on Some Assumptions:

- Molecules are in constant random motion
- There are vast spaces between gas molecules
  - Molecules considered "volumeless"
  - Move easily when force is applied
  - No interaction between molecules



- Collisions are Elastic
  - No gain or loss of energy
- Average kinetic energy is proportional to temp. in Kelvins
  - Molecules move faster as temp increases

According to theory:

- Pressure is created by molecules hitting the walls
- Amount of pressure depends on frequency & strength of collisions

Boyle's Law: Pressure/Volume Relationship

For a fixed amount of gas at constant temperature, volume decreases as pressure increases (**inverse relationship**)

PV = constant so $P_1V_1 = P_2V_2$

Rearranging equation:

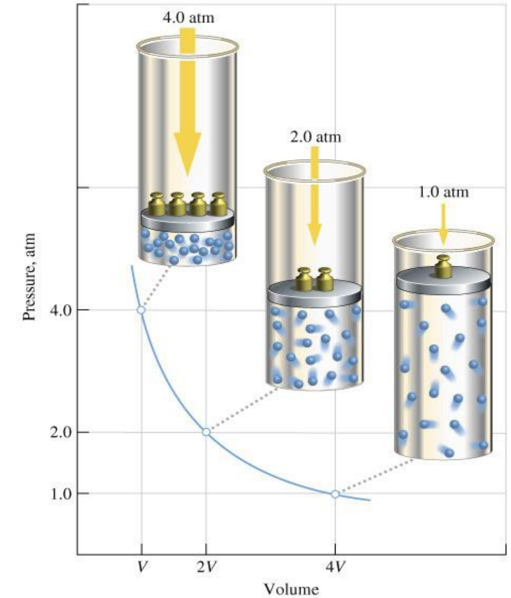
$$P_1 = \frac{P_2V_2}{V_1} \qquad V_1 = \frac{P_2V_2}{P_1}$$

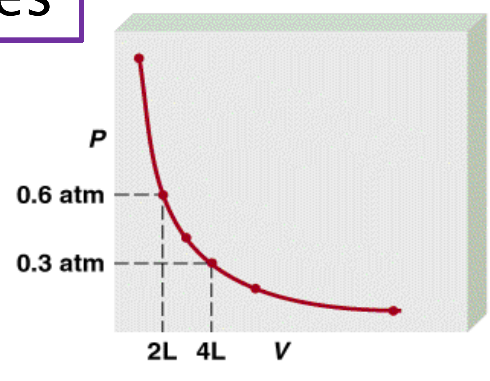
↑pressure: ↓volume

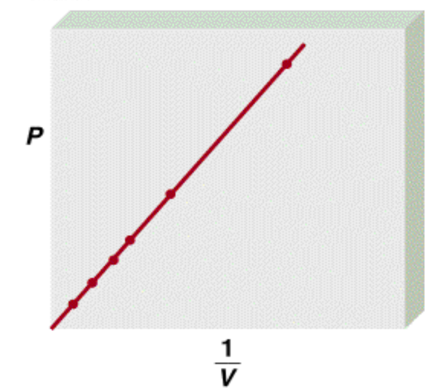
Reduce space between molecules

↓volume: ↑pressure

Increase molecule-wall collisions



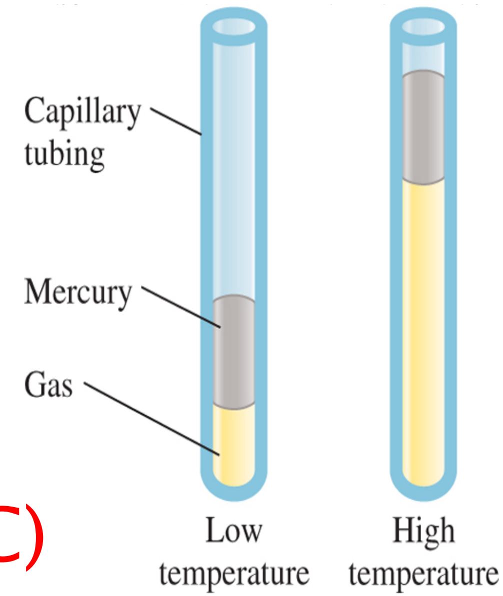




Charles' Law: Volume/Temp. Relationship

For a fixed amount of gas at constant pressure, volume increases as temperature increases **(direct relationship)**

V/T= constant so $V_1/T_1 = V_2/T_2$

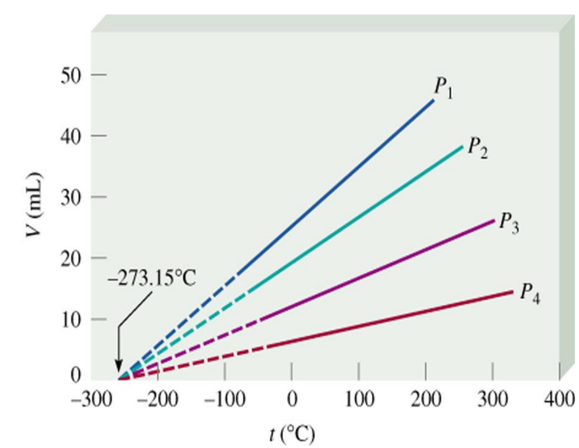


Rearranging equation:

$$V_1 = \frac{V_2 T_1}{T_2} \qquad T_1 = \frac{T_2 V_1}{V_2}$$

Temp. in **kelvins (K)**, not Celsius (°C)

T (K) = ºC + 273.15



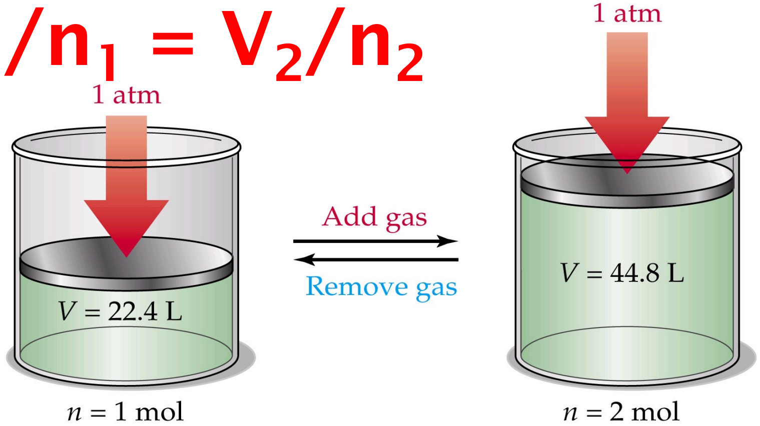
As temperature increases:

- Molecules move faster
- They hit the wall harder
- Volume increases to hold pressure

Avogadro's law: Moles/Volume Relationship

At fixed temperature and pressure, the volume of a gas depends on the # of moles of gas present

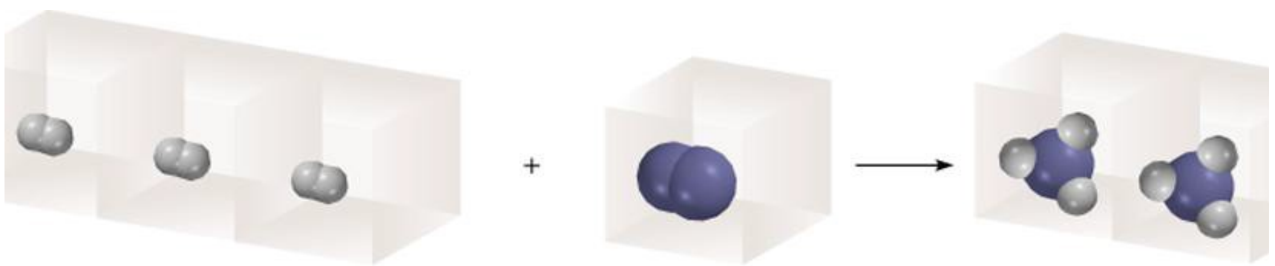
V/n= constant so $V_1/n_1 = V_2/n_2$



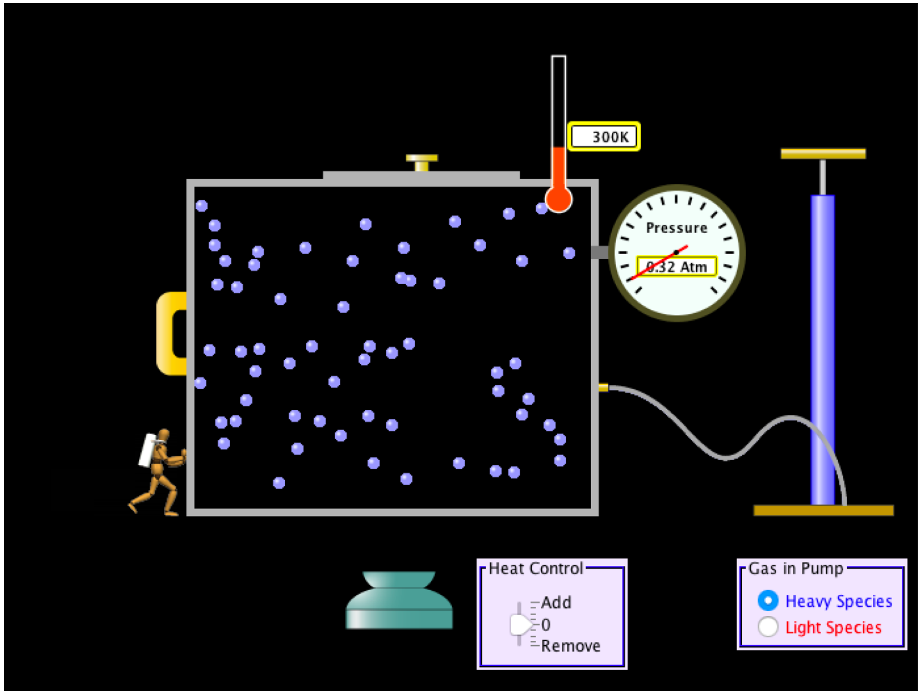
Rearranging equation:

$$V_1 = \frac{V_2 n_1}{n_2} \qquad n_1 = \frac{n_2 V_1}{V_2}$$

More molecules need more space to maintain the same pressure and temperature



$3H_2\,(g)$	+	$N_2\,(g)$	→	$2NH_3\,(g)$
3 molecules	+	1 molecule	→	2 molecules
3 moles	+	1 mole	→	2 moles
3 volumes	+	1 volume	→	2 volumes



https://phet.colorado.edu/en/simulation/legacy/gas-properties

The Combined Gas Law & the Ideal Gas Constant

Combines all three laws

Boyles Law	constant = PV
Charles's Law	constant = V / T
Avogadro's Law	constant = V / n

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

Standard Temperature and Pressure (STP) = 1atm & 273K

$$\frac{P_1V_1}{n_1T_1} = \frac{1atmx22.4L}{1molx273K} = \frac{0.0821Latm}{molK} = R$$

Ideal Gas Constant: $R = \frac{0.0821Latm}{mol\,K}$

Ideal Gas Law: $\boxed{PV = nRT}$

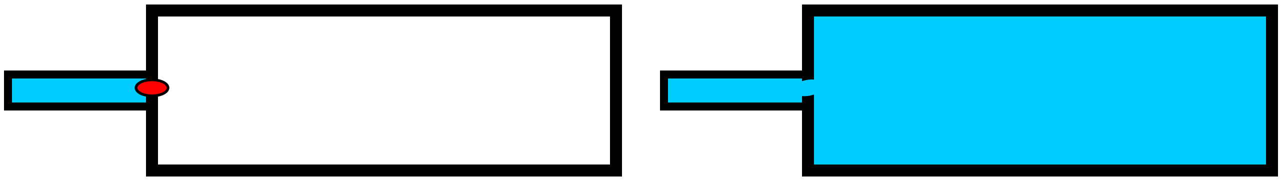
The Universal Gas Constant - *R* - in alternative Units

- atm•cm^3/(mol•K) : 82.0575
- atm•ft^3/(lbmol•K) : 1.31443
- atm•ft^3/(lbmol•^{o}R) : 0.73024
- atm•l/(mol•K) : 0.08206
- bar•cm^3/(mol•K) : 83.14472
- bar•l/(mol•K) : 0.08314472
- Btu/(lbmol•^{o}R) : 1.9859
- cal/(mol•K) : 1.9859
- erg/(mol•K) : 83144720
- hp•h/(lbmol•^{o}R) : 0.0007805
- inHg•ft^3/(lbmol•^{o}R) : 21.85
- J/(mol•K) : 8.314462
- (kgf/cm^2)•l/(mol•K) : 0.084784
- kPa•cm^3/(mol.K) : 8314.472
- kWh/(lbmol•^{o}R) : 0.000582
- lbf•ft/(lbmol•^{o}R) : 1545.349
- mmHg•ft^3/(lbmol•K) : 999
- mmHg•ft^3/(lbmol•^{o}R) : 555
- mmHg•l/(mol•K) : 62.364
- Pa•m^3/(mol•K) : 8.314472
- psf•ft^3/(lbmol•^{o}R) : 1545.349
- psi•ft^3/(lbmol•^{o}R) : 10.73
- Torr•cm^3/(mol•K) : 62364
- kJ/(kmol•K) : 8.314462

Units used in ideal gas equation must match R used

A 4.50-L cylinder containing He(g) at an unknown pressure is connected to a 92.5-L evacuated cylinder. When the connecting valve between the two cylinders is opened, the pressure falls to 1.40 atm. What was the pressure in the 4.50-L cylinder?

Initial Conditions (P_1V_1) Final Conditions (P_2V_2)



A = 30.2 atm

Decreasing the temperature of 10.00 L of H_2 (g) from 25°C to -77°C decreases its volume to what value?

A = 6.58 L

Sulfur hexafluoride (SF_6) is a colorless and odorless gas. Due to its lack of chemical reactivity, it is used as an insulator in electronic equipment. Calculate the pressure (in atm) exerted by 1.39 moles of the gas in a steel vessel of volume 6.09 L at 55°C.

A = 6.15 atm

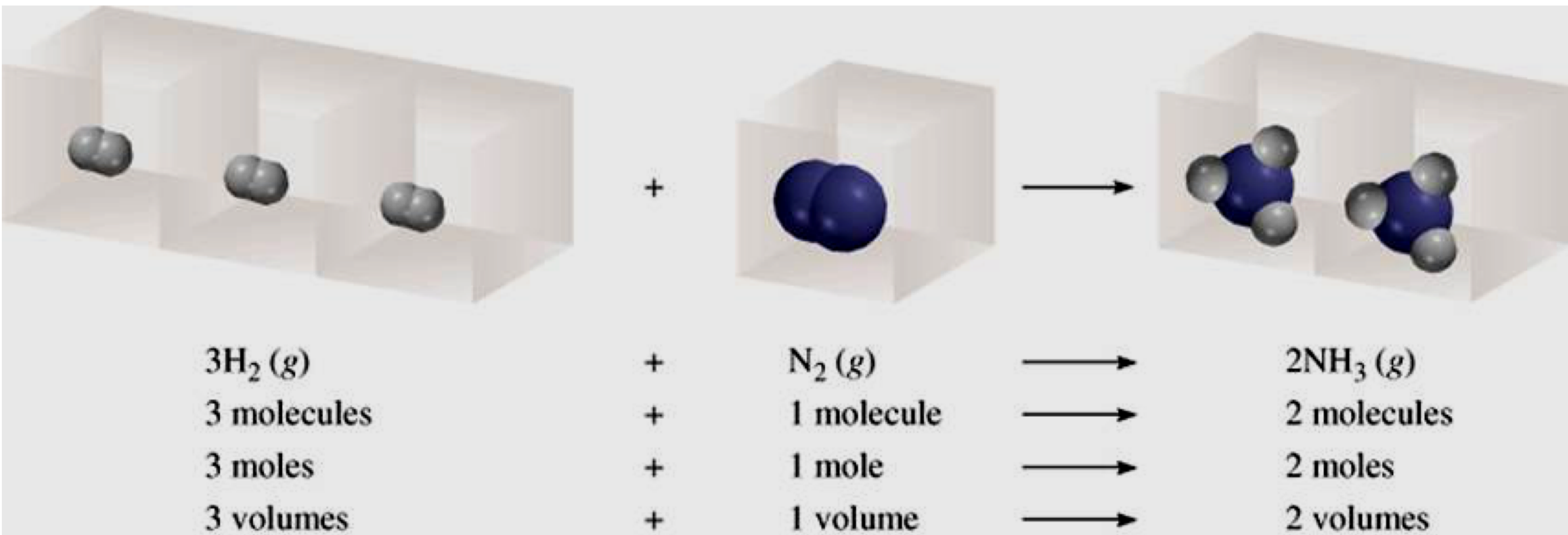
Identify the noble gas if 23.6 g exerts a pressure of 1293 torr at 37°C in a 17.5-L container.

A = Neon (20.2 g/mol)

The Law of Combining Volumes

At the same T and P, the volume of a gas is directly related to the moles of gas and the number of molecules of a gas.

The ratio is the same as that in the chemical equation



Gases ONLY!

Relationship requires there to be NO CHANGE in T & P

Ammonia burns in oxygen to form nitric oxide (NO) & water vapor. How many liters of NO are obtained from 1.0 liter of ammonia at the same temperature and pressure? How many liters of water vapor are obtained?

Write the balanced chemical equation

Get the volume ratio from the balanced equation

Use volume ratio to convert 1 liter of NH_3 to vol. NO

A = 1.0 L NO; 1.5 L H_2O

Using STP values for ideal gases as conversion factors:

At STP (1 atm, O°C) 1 mole of an ideal gas occupies 22.4 L

What is the Mass of 16.2 L of SF_6 at STP?

A = 106 g

Determine the volume in liters of NO(g) that will be produced from 5.25 L of 0_2 (g) and excess NH_3(g) at constant pressure and temperature.

$$4\ NH_3\ (g) + 5\ O_2\ (g) \rightarrow 4\ NO\ (g) + 6\ H_2O\ (l)$$

Using 1 mol = 22.4 L as a conversion factor

Using the Law of Combining Volumes to get volume of NO

A = 4.20 L regardless of method

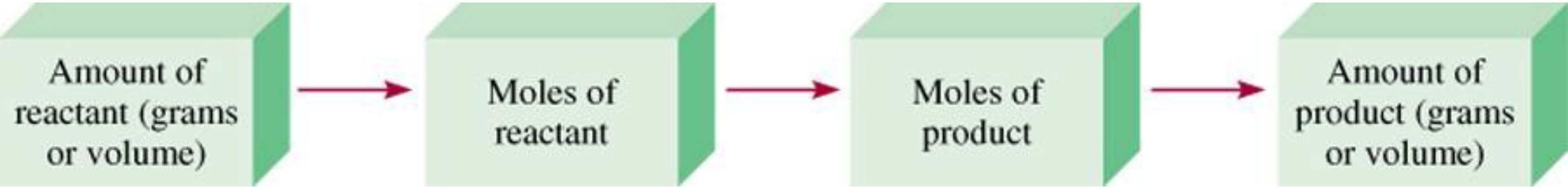
A 16.4-g sample of a gas at 25.0 psi and 25.0°C is confined in a 17.5 L container. This gas is moved to a 28.5 L container at 100.0°C and 14.0 psi.
How much gas was removed or added?

Changing conditions, so equation is:

Note: Temperature must be converted to Kelvin, but since the units will cancel, the other units can be used as given.

A = 4.5g removed

Gas Stoichiometry



What is the volume of CO_2 produced at 37^0 C and 1.00 atm when 5.60 g of glucose (180.15768g/mol) are used up in the Reaction?

$$C_6H_{12}O_6\ (s) + 6O_2\ (g) \longrightarrow 6CO_2\ (g) + 6H_2O\ (l)$$

$$g\ C_6H_{12}O_6 \longrightarrow mol\ C_6H_{12}O_6 \longrightarrow mol\ CO_2 \longrightarrow V\ CO_2$$

A: 4.75 L

Additional Practice

Stoichiometry and Gas Laws

What volume in liters of CO (g) at 250ºC and 0.904 atm is produced from 453.6g Fe_2O_3 (s) in the following reaction:

$$Fe_2O_3\,(s) + 3C\,(s) \rightarrow 2Fe\,(s) + 3\,CO\,(g)$$

A: 405 L

Mixtures of Gases: Dalton's Law of Partial Pressures

Total Pressure = the sum of the partial pressures.

$$P_{total} = P_1 + P_2 + P_3 + \cdots$$

Partial Pressure = the pressure exerted by each individual gas in the container.

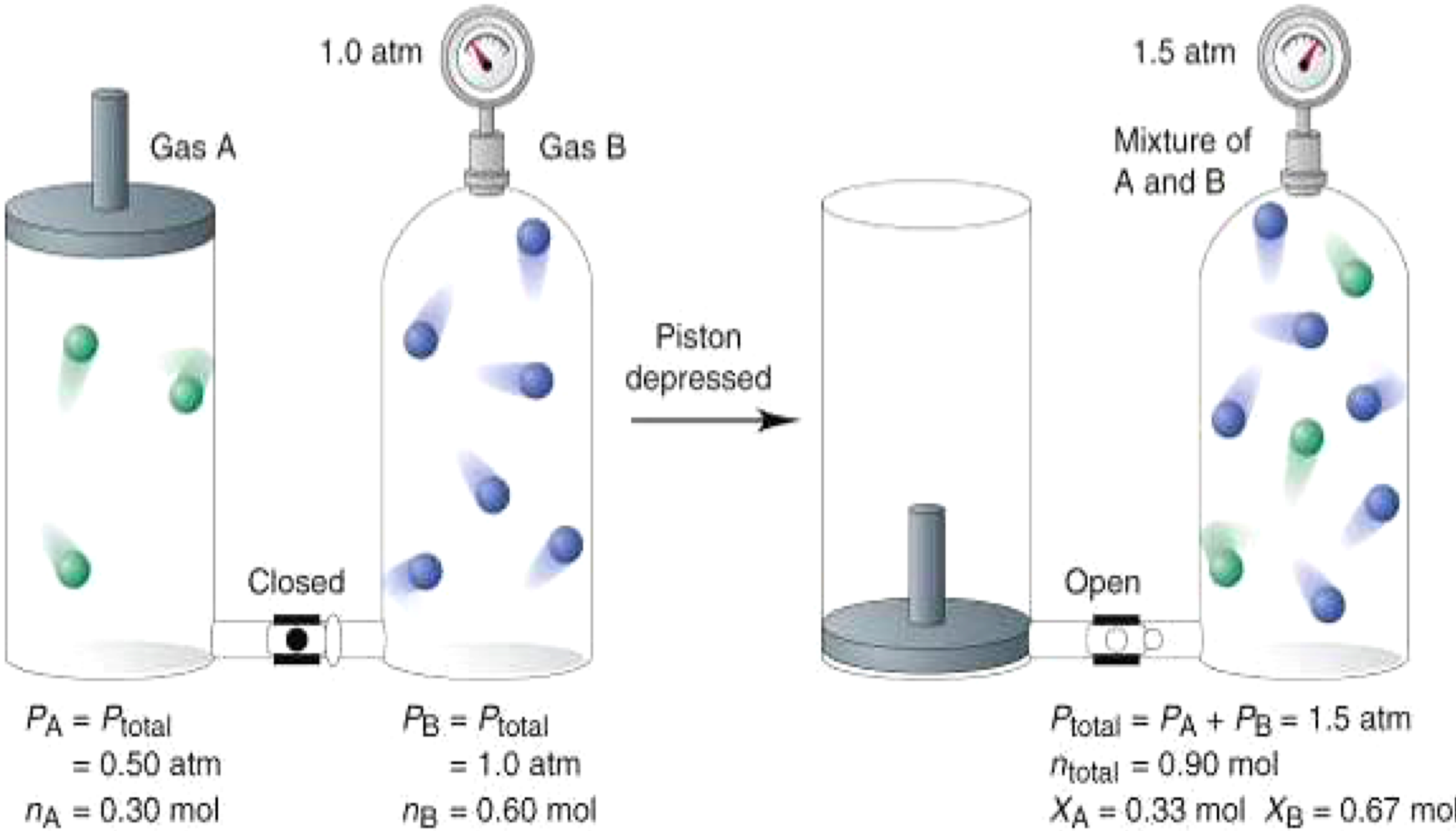
$$P_1 = (n_1RT)/\ V; \quad P_2 = (n_2RT)/\ V; \text{ etc.}$$

Mole Fraction = the moles of a given type of gas in a mixture divided by the total number of moles.

$$P_1/P_{total} = n_1/n_{total} = x_1$$

Partial Pressure = $P_1 = x_1 \cdot P_{total}$

Mixtures of Gases
Dalton's Law of Partial Pressures



A sample of natural gas contains 8.24 moles of CH_4, 0.421 moles of C_2H_6, and 0.116 moles of C_3H_8. If the total pressure of the gases is 1.37 atm, what is the partial pressure of propane (C_3H_8)?

A = 0.0181 atm

Collection of Gases Over Water

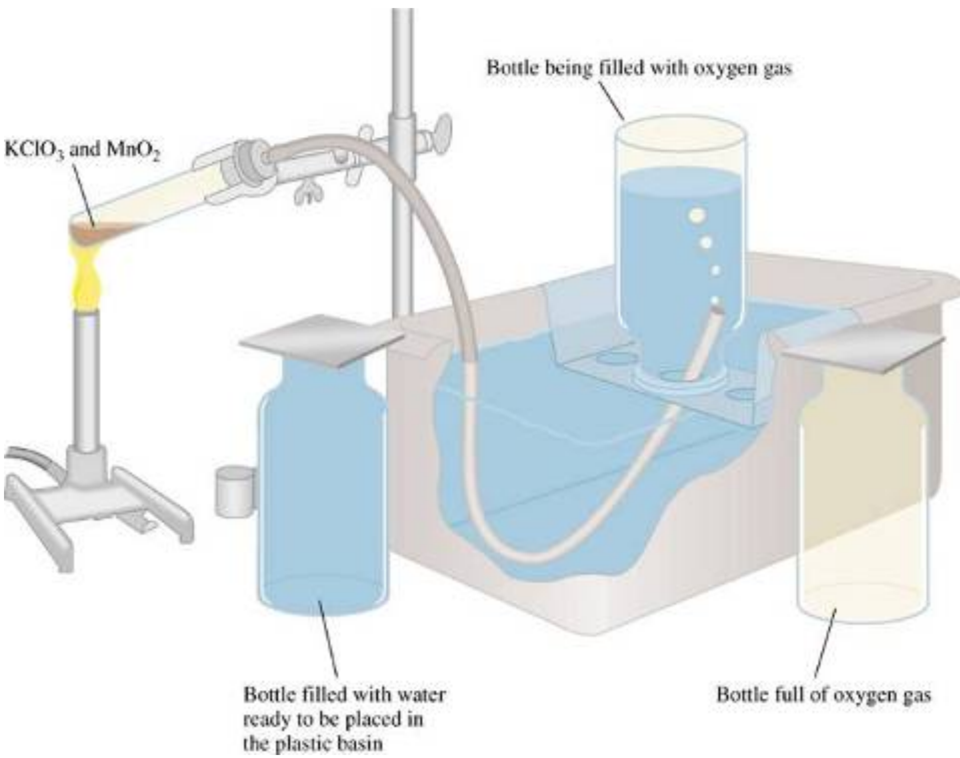
A gas is collected into a container of water

- Water saturated gas rises and displaces liquid water

Water is present in the gas phase above the liquid water

- The vapor pressure of the water must be subtracted from the measured pressure of the gas

$P_{total} = P_{atm} = P_{gas} + P_{water(g)}$ $\quad$ $P_{gas} = P_{atm} - P_{water(g)}$

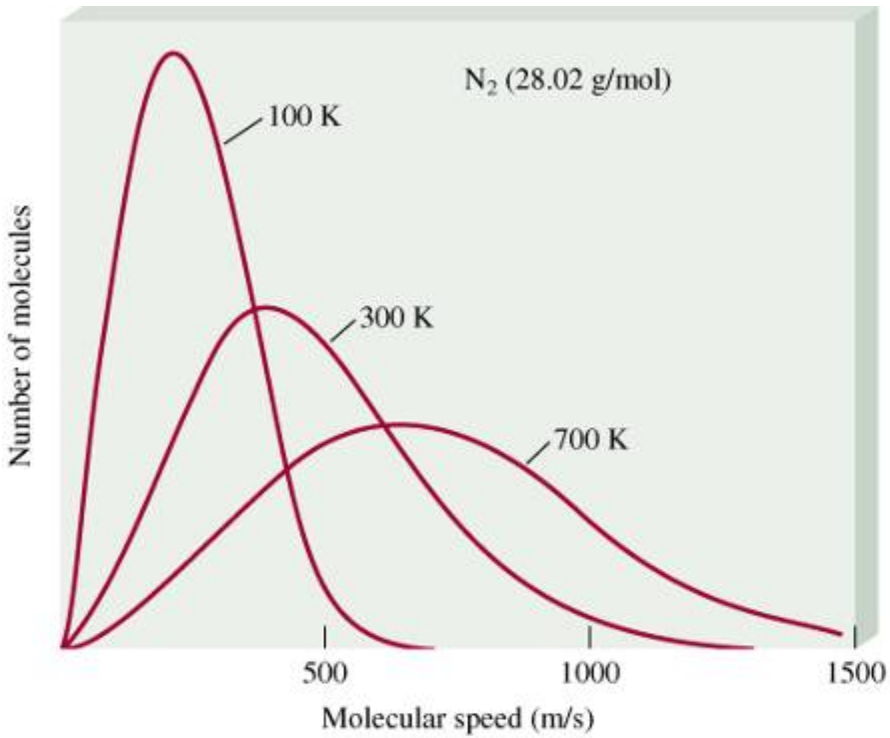


Temperature (°C)	Water Vapor Pressure (mmHg)
0	4.58
5	6.54
10	9.21
15	12.79
20	17.54
25	23.76
30	31.82
35	42.18
40	55.32
45	71.88
50	92.51

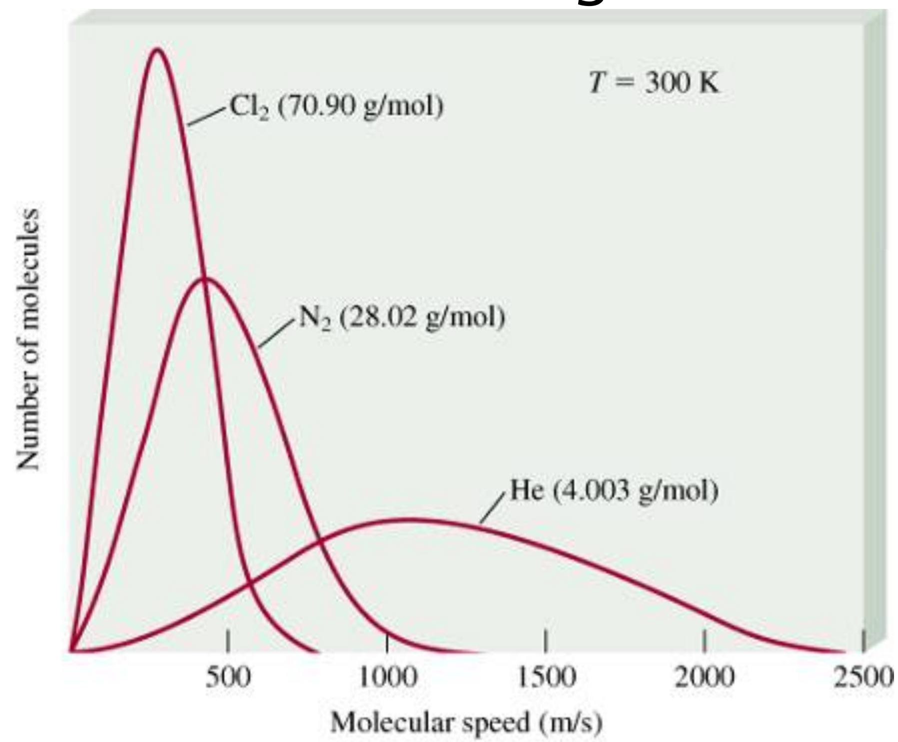
Molar Mass & Temperature Effects: Root-Mean-Squared Speed

$$\sqrt{u_2} = u_{rms} = \sqrt{\frac{3RT}{MolarMass}}$$

At Higher temperatures molecules move faster



Small molecules move faster than big ones



Calculation of v_{rms}

What is the v_{rms} of diatomic nitrogen at 20°C?

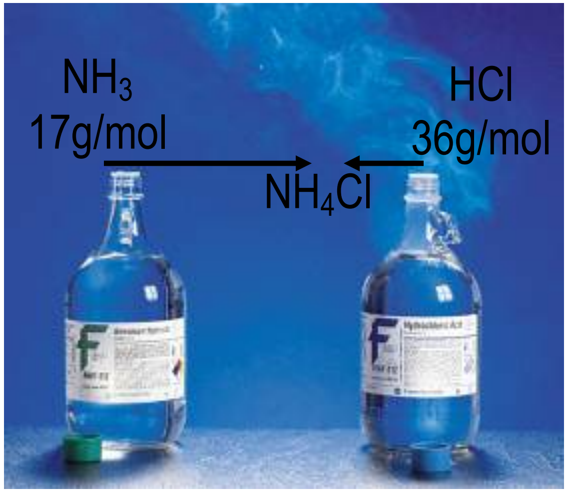
R = 8.314 J/mol K

$$\sqrt{u_2} = u_{rms} = \sqrt{\frac{3RT}{MolarMass}}$$

A = 511 m/s

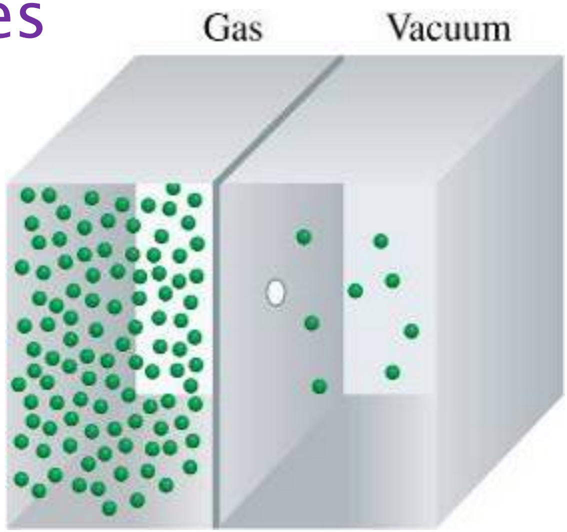
Diffusion and Effusion

Diffusion is the process by which one gas mixes with another as a result of molecular movement



$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \sqrt{\frac{MolarMass_2}{MolarMass_1}}$$

NH_4Cl collects closer to HCl
HCl molecules larger than NH_3 molecules



Effusion is the process in which a gas under pressure escapes from its container through a small hole.

Reality: The Van der Waal's Equation

- Most gases show deviations from ideal behavior.
- Assumptions of the kinetic-molecular theory not exact

- At high pressure/density gases act more like liquids/solids
  - Attractive forces between molecules increase
  - Molecular volume no longer negligible

Van der Waal's equation:

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

a = Molecular attraction correction coefficient

- Actual P is higher than the measured P
- $P_{actual} = P + an^2/V^2$

b = Volume correction coefficient

- Actual V is lower than the container V
- $V_{actual} = V\text{-}nb$

van der Waals Constants of Some Common Gases

Gas	a $\left(\frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2}\right)$	b $\left(\frac{\text{L}}{\text{mol}}\right)$
He	0.034	0.0237
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0266
H_2	0.244	0.0266
N_2	1.39	0.0391
O_2	1.36	0.0318
Cl_2	6.49	0.0562
CO_2	3.59	0.0427
CH_4	2.25	0.0428
CCl_4	20.4	0.138
NH_3	4.17	0.0371
H_2O	5.46	0.0305

Larger & more polar = less ideal

Carbon dioxide gas (1.00 mole) at 373 K occupies 536 mL & reads 50.0 atm pressure. What is the calculated pressure using:

(i) Ideal gas equation?

(ii) van der Waals equation?

Calculate the % deviation of each value from that observed.

van der Waals constants for CO_2: $a = 3.592\ L^2\ atm\ mol^{-2}$

$b = 0.04267\ L\ mol^{-1}$

(i) Using the Ideal Gas Equation: PV = nRT

V = 0.536 L

T = 373 K

N = 1.00 mol

R = 0.0821 L atm / mol K

$P = nRT/V = [(1.00\ mol)(0.0821\ L\ atm/mol\ K)(373\ K)]/0.536\ L$

P = 57.1 atm

% deviation = [(50.0 atm – 57.1 atm)/50.00 atm] x 100

% deviation = 14.2 %

(ii) Using Van der Waals equation:

$$[P + a(n^2/V^2)][V - (nb)] = nRT$$

$$[P + 3.592 \times (1.00/0.536)^2][0.536 - (1.00 \times 0.04267)] = (1.00 \times 0.082057 \times 373)$$

$$(P + 12.5028)(0.49333) = 30.607261$$

$$P + 12.5028 = 62.04216$$

$$P = 49.5394 \text{ atm}$$

$$\% \text{ deviation} = [(50.0-49.5)/50] \times 100$$

% deviation = 1.00%

Ideal: 14.2 % vs. van der Waals: 1.00%