

GASES

Lecture 10



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SCOPE OF THIS LECTURE

- Properties of gases
- Ideal gas equation
- Kinetic molecular theory
- Real gases



GAS PROPERTIES

Volume of gas

V

Fills its container

Variable volume (e.g. balloon)

Fixed volume (e.g. glass container)

Usual unit m^3 or dm^3 (L)

Temperature of gas

T

Measure of direction of heat flow

‘How hot is something’

Units issues:

K essential unit for all relationships

$$K = ^\circ\text{C} + 273.15$$

Pressure of gas

p



GAS PROPERTIES

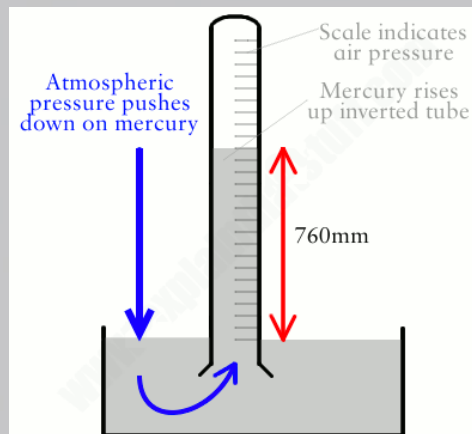
Pressure of gas

P

Pressure is defined as *force per area*

Force of gas particles colliding with any object that can experience this pressure

Barometer is used to measure external pressure

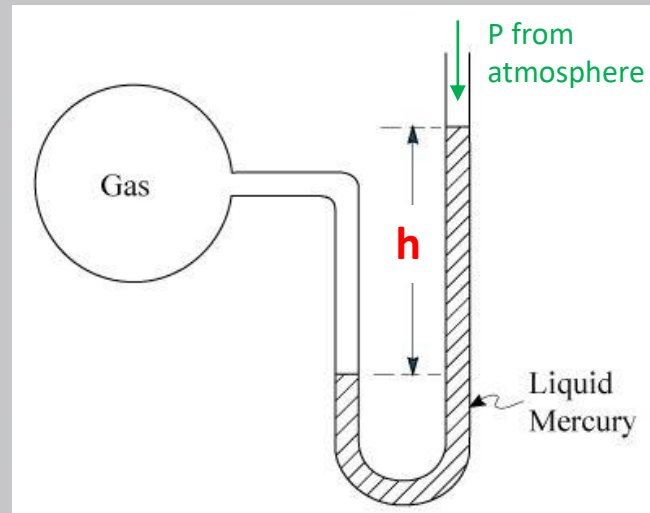


Height of column associated with pressure

Water = 30 feet at sea level

Mercury = about 30 inches or 760 mmHg

Manometer (open-ended)



h is the difference between the pressure of the gas sample and that of the atmosphere

$$\text{gas } P = P(\text{atm}) + h$$

In this case, as gas pushes mercury further, gas has more pressure

Various Units of P

mmHg (torr)

Atmospheres (atm)

1 atm = 760 torr

Pascal ($\text{kg}(\text{m}^{-1}\text{s}^{-2})$) Pa

101,325 Pa = 1 atm

Bar ($\text{kg}(\text{m}^{-1}\text{s}^{-2})$)

1 bar = 100,000 Pa

SAMPLE PROBLEM

$$1 \text{ atm} = 101.3 \text{ kPa} = 101,325 \text{ Pa} = 760 \text{ mm Hg} = 760 \text{ torr} = 14.7 \text{ lb/in}^2 \text{ (psi)}$$

EXAMPLE 1: The air pressure for a certain tire is 109 kPa. What is this pressure in atmospheres?

EXAMPLE 2. An experiment at Sandia National Labs in New Mexico is performed at atmospheric pressure of 758.7 mm Hg. What is this pressure in atm?

EXAMPLE 3: A bag of potato chips is sealed in a factory near sea level. The atmospheric pressure at the factory is 761.3 mm Hg. The pressure inside the bag is the same. What is the pressure inside the bag of potato chips in Pa?



PRACTICE PROBLEMS:

$$1 \text{ atm} = 101.3 \text{ kPa} = 101,325 \text{ Pa} = 760 \text{ mm Hg} = 760 \text{ torr} = 14.7 \text{ lb/in}^2 \text{ (psi)}$$

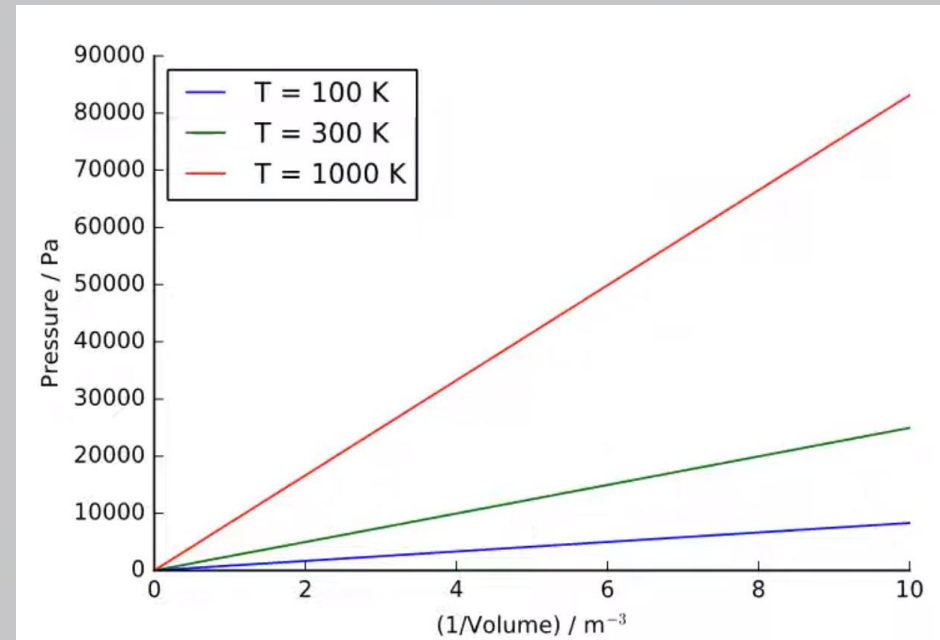
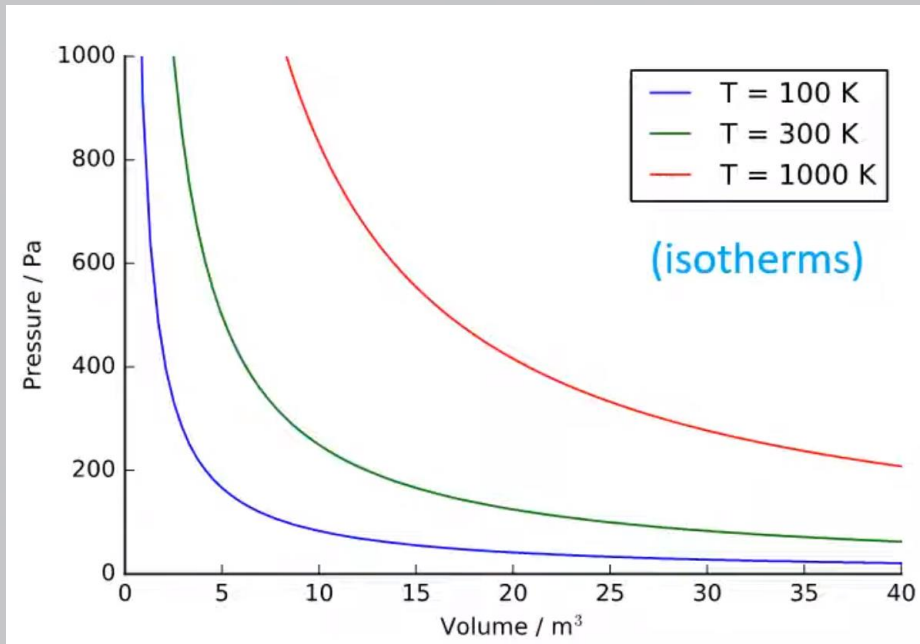
PROBLEM 1: The weather news gives the atmospheric pressure as 1.07 atm. What is this atmospheric pressure in torr?

PROBLEM 2: The same bag of potato chips from Problem 5 is shipped to a town in Colorado, where the atmospheric pressure is 99.82 kPa. What is the difference (in Pa) between the pressure in the bag and the atmospheric pressure of the town?



GAS LAWS - RELATIONSHIPS BETWEEN **V**, **T** AND **P**

Boyle's Law



P related to **V**
?

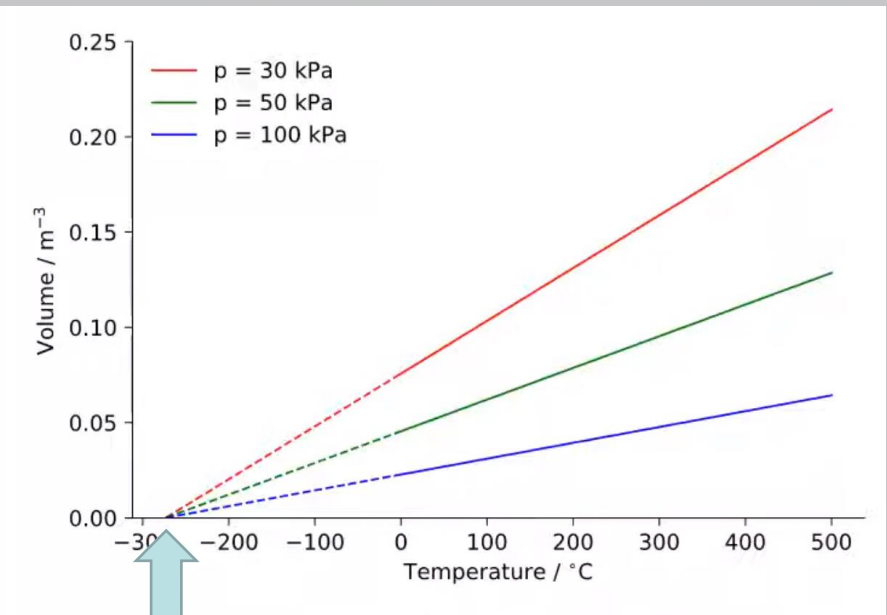
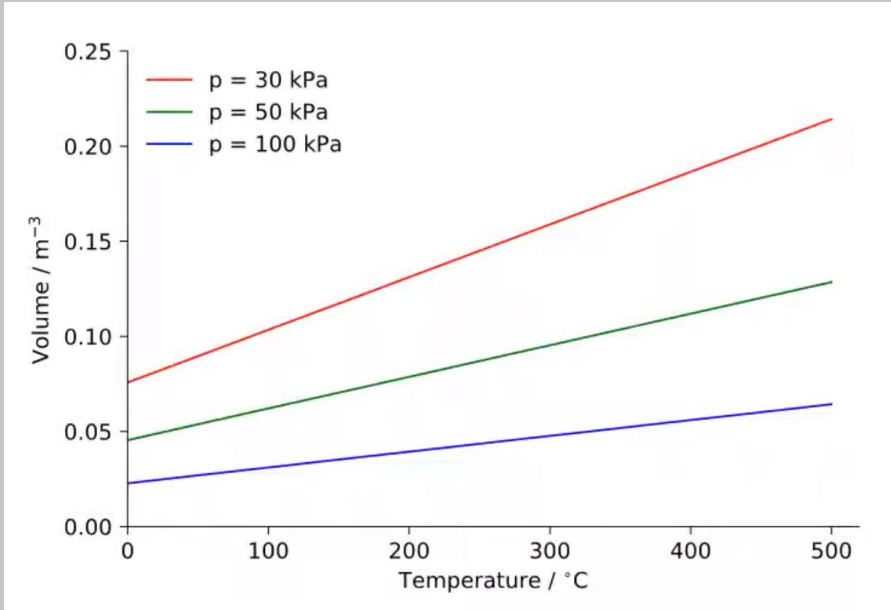
P proportional to **1/V**
P = constant x T x **1/v**



The pressure of fixed amount of gas at constant temperature is inversely proportional to the volume

RELATIONSHIPS BETWEEN V, T AND P

Charles' Law



V proportional to T
V = constant x T + another constant

absolute 0
-273.15 °C

Limit of temperatures
0 Kelvin

The volume of a fixed amount of gas at constant pressure is directly proportional to the absolute temperature

V proportional to T
V = constant x T
T in Kelvins



RELATIONSHIPS BETWEEN V, T AND P

Boyle's Law: Volume and Pressure inversely proportional (constant T)

P up V down

P down V up

Charles's Law: Volume and Temperature proportional (constant P)

T up V up

T down V down

Gay-Lussac's Law: Temperature and Pressure proportional (constant V)

P up T up

P down T down



SAMPLE PROBLEM

A gas occupies a volume of **3.5 L** at **25 °C** and **1.2 bar** pressure. Calculate the volume when the temperature is lowered to **10 degC** at the **same pressure**.

Charles's Law: T down V down
so smaller temp on top

$$25\text{ °C} = 298\text{ K}$$

$$10\text{ °C} = 283\text{ K}$$

$$\text{new volume} = \text{old volume} \times \left[\frac{283}{298} \right]$$

$$\text{new volume} = 3.5\text{ L} \times \left[\frac{283}{298} \right]$$

$$\text{new volume} = 3.32\text{ L}$$



A gas occupies a volume of **3.5 L** at **25 °C** and **1.2 bar** pressure. Calculate the volume when the pressure is lowered to **0.90 bar** at the **same temperature**.

Boyle's Law: P down V up
so bigger pressure on top

$$\text{new volume} = \text{old volume} \times \left[\frac{1.2}{0.9} \right]$$

$$\text{new volume} = 3.5\text{ L} \times \left[\frac{1.2}{0.9} \right]$$

$$\text{new volume} = 4.67\text{ L}$$

SAMPLE PROBLEM

A gas occupies a volume of 3.5 L at 25 °C and 1.2 bar pressure. Calculate the pressure when the temperature is lowered to 10 °C and the gas is compressed to a volume of 2.5 dm³.

Boyle's Law:

V down then P up so bigger volume on top

Gay-Lussac's Law:

T down then P down so smaller temp on top

$$25\text{ °C} + 273.15 = 298\text{ K}$$

$$10\text{ °C} = 283\text{ K}$$

$$\text{new pressure} = \text{old pressure} \times \left[\frac{3.5}{2.5} \right] \times \left[\frac{283}{298} \right]$$

$$\text{new pressure} = 1.2 \times \left[\frac{3.5}{2.5} \right] \times \left[\frac{283}{298} \right]$$

$$\text{new pressure} = 1.57\text{ bar}$$



PRACTICE PROBLEMS

PRACTICE PROBLEM 1: A gas occupies 0.81 litres at 0.887 bar pressure. What is the volume when the pressure is changed to 0.815 bar at a constant temperature?

PRACTICE PROBLEM 2: A 7.41 L sample of dry air is cooled from 68.1 °C to 10 °C while the pressure is maintained at 285 kPa. What is the final volume in L to 2 decimal places?

PRACTICE PROBLEM 3: A small cylinder of helium gas has a volume of 2.0 L and a pressure of 10.0 atm at 26 degC. If all the gas in the cylinder is used to fill a single large balloon at 2.0 atm and the same temperature, to what volume does the balloon inflate?



PRACTICE PROBLEM 4: A gas occupies 3.74 liters at 0.540 atm pressure and 317 K temperature. What is the volume when the pressure is changed to 0.431 atm and the temperature becomes 261 K.

AVOGADRO's HYPOTHESIS

For a fixed **temperature** and **pressure**, equal **volumes** of gases contain the same number of molecules

Volume of any gas is proportional to **number of moles** at a given **T** and **P**

Avogadro

$$V \propto n$$

Boyle

$$V \propto 1/P$$

$$V \propto nT/P$$

$$PV \propto nT$$

Charles

$$V \propto T$$

$$PV = nRT$$

IDEAL GAS LAW

- ideal gas is a gas that obeys this law under all conditions
- there are no interactions between gas molecules
- it is a good approximation of the behaviour of many gases under many conditions



IDEAL GAS LAW – R and MOLAR VOLUME

$$PV = nRT$$

Value of R depends on units of P and V

P Pa V m ³	R = 8.314 Pa m ³ mol ⁻¹ K ⁻¹ R = 8.314 J mol K ⁻¹
P bar V m ³	R = 8.314 x 10 ⁻⁵ bar m ³ mol ⁻¹ K ⁻¹
P bar V dm ³ (L)	R = 0.08314 bar dm ³ mol ⁻¹ K ⁻¹
P atm V dm ³ (L)	R = 0.08206 atm L mol ⁻¹ K ⁻¹
P torr V dm ³ (L)	R = 62.36 torr L mol ⁻¹ K ⁻¹

Standard Temperature and Pressure **STP**

0 °C (273.15 K)
1 atm

$$PV = nRT$$

$$(1 \text{ atm}) V = (1 \text{ mol}) (0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1}) (273.15 \text{ K})$$

Molar Volume = 22.4 L (dm³)

Standard Ambient Temperature and Pressure **SATP**

25 °C (298.15 K)
1 bar

$$PV = nRT$$

$$(1 \text{ bar}) V = (1 \text{ mol}) (0.08314 \text{ bar dm}^3 \text{ mol}^{-1} \text{ K}^{-1}) (298.15 \text{ K})$$

Molar Volume = 24.8 L (dm³)



IDEAL GAS LAW – MOLAR MASS and GAS DENSITY

Dumas Method of **Molar Mass** Determination:

1.47 g of an unknown gas occupies 130 mL at 20 °C and 740 mmHg. Calculate the molar mass.

$P = 740 \text{ mmHg} = 740/760 = 0.974 \text{ atm}$
 $V = 130 \text{ mL} = 0.130 \text{ L}$
 $T = 20 \text{ }^{\circ}\text{C} = 20 \text{ }^{\circ}\text{C} + 273.15 = 293.15 \text{ K}$
 $g = 1.47 \text{ g}$

$PV = nRT$

$(0.974 \text{ atm})(0.130 \text{ L}) = (n \text{ mol})(0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})(293.15 \text{ K})$

$n = 5.26 \times 10^{-3} \text{ mol}$
 $g = n \times \text{MM}$
 $1.47 \text{ g} = (5.26 \times 10^{-3} \text{ mol}) \times \text{MM}$

MM = 279 g/mol



Density of gases:

$g = n \times \text{MM}$

$PV = nRT$

$PV = \frac{gRT}{\text{MM}}$

$\frac{g}{V} = \frac{P\text{MM}}{RT}$

density	up	P up
density	up	MM up
density	down	T up

‘heavier than air’
Hot air balloon

SAMPLE PROBLEM

$$PV = nRT$$

EXAMPLE 1: Calculate the volume occupied by 10.0 g of NH_3 gas at STP

EXAMPLE 2: Consider the reaction, $2 \text{C}_2\text{H}_6 (\text{g}) + 7 \text{O}_2 (\text{g}) \rightarrow 4 \text{CO}_2 (\text{g}) + 6 \text{H}_2\text{O} (\text{g})$. How many g of $\text{O}_2 (\text{g})$ would react with 20.0 L of $\text{C}_2\text{H}_6 (\text{g})$ at 25 °C and 740 torr pressure?

STEP 1: Calculate moles of C_2H_6

STEP 2: Find the corresponding moles of oxygen

STEP 3: Find the mass of O_2

EXAMPLE 3: What mass of CO_2 will exert the same pressure as 12 g of hydrogen sulfide, H_2S , in the same container under the same conditions.



SAMPLE PROBLEM

EXAMPLE 1: A 355-mL container holds 0.146 g Ne and an unknown amount of Ar at 35°C and a total pressure of 626 mmHg. Calculate the moles of Ar present.

- a) 4.33×10^{-3} mol Ar
- b) 8.79 mol Ar
- c) 0.0116 mol Ar
- d) 7.23×10^{-3} mol Ar
- e) 1.16 mol Ar

EXAMPLE 2: What is the density of Freon-11 (CFCl_3) at 120 °C and 1.5 atm?

- a) 5.23 g/L
- b) 0.192 g/L
- c) 52.3 g/L
- d) 6.39 g/L
- e) 1.92 g/L

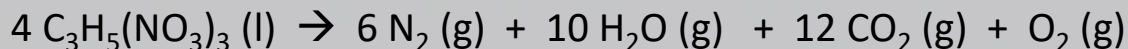


PRACTICE PROBLEMS

PRACTICE PROBLEM 1: A 100 mL flask contains argon at 1.3 atm and 77 degC. What amount of Ar is present (in grams)?

PRACTICE PROBLEM 2: What volume will 0.361 g of air with an average molar mass of 28.97 g/mol occupy in the troposphere when the pressure is 1.22 atm at 25 degC.

PRACTICE PROBLEM 3: Nitroglycerin is a shock-sensitive liquid that detonates by the reaction



Calculate the volume of CO_2 gas produced at 150 kPa and 100 degC from the detonation of 1.0 g of nitroglycerin



DALTON'S LAW OF PARTIAL PRESSURES

$$PV = nRT$$

n can also represent moles of ALL mixed gases !!!

Calculate the pressure for each of the following gases: 32.0 g O₂ (g), 56.0 g N₂ (g), and 28.0 g of He (g) in a 10.0 L flask at 293 K.

$$P = \frac{nRT}{V} = \frac{1 \text{ mol} \times 0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1} \times 293 \text{ K}}{10.0 \text{ L}} \quad (0.08206 \text{ atm L mol}^{-1} \text{ K}^{-1})$$

$$32.0 \text{ g of O}_2 = 1.0 \text{ mol O}_2 (\text{g})$$

$$P \text{ O}_2 (\text{g}) = 2.41 \text{ atm} = (1/10) \times 24.1$$

$$56.0 \text{ g of N}_2 = 2.0 \text{ mol N}_2 (\text{g})$$

$$P \text{ N}_2 (\text{g}) = 4.82 \text{ atm} = (2/10) \times 24.1$$

$$28.0 \text{ g of He} = 7.0 \text{ mol He (g)}$$

$$P \text{ He (g)} = 16.84 \text{ atm} = (7/10) \times 24.1$$

total 10.0 mol

total 24.1 atm



DALTON'S LAW

In a mixture of non-reacting gases, the total pressure exerted is equal to the sum of the partial pressures of the individual gases

$$P (\text{total}) = \Sigma P (\text{partial})$$

The partial pressure of each gas is equal to the total pressure multiplied by the mole fraction of that gas

$$P (\text{partial}) = P (\text{total}) \times \chi (\text{gas})$$



PRACTICE PROBLEMS

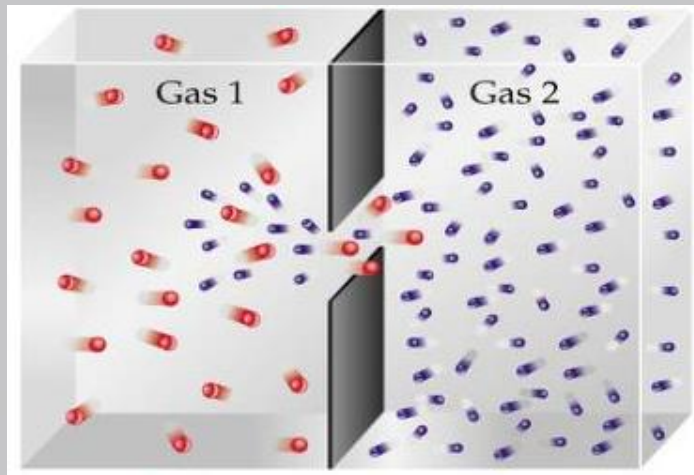
PRACTICE PROBLEM 1: calculate the partial pressure of each gas and the total pressure of the following mixture that occupies 500 mL at 0 degC: 0.020 mol N_2 and 2.33 g of O_2 .

PRACTICE PROBLEM 2: A sample of dry air of total mass 1.0 g consists of 0.76 g of nitrogen and 0.24 g of oxygen.

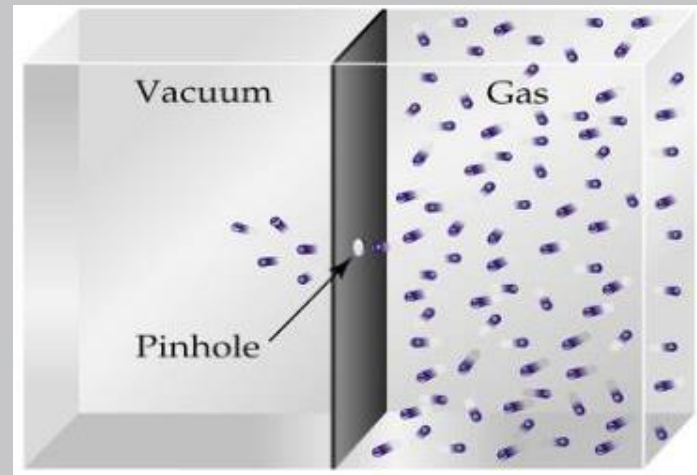
- Calculate the partial pressures of these gases and the total pressure in atm when this sample is in flask of volume 1.00 L at 20 degC
- The sample of air is heated until the total pressure is 1.00 atm. What are the partial pressures of oxygen and nitrogen in the heated sample.



GRAHAM'S LAWS



DIFFUSION: different gases mix



EFFUSION: gas escapes through a hole

Average velocity of gas is inversely proportional to the square root of the molar mass

$$\text{average velocity} \propto 1 / \sqrt{\text{MM}}$$

velocity - u



GRAHAM'S LAWS - EXAMPLES

How much faster will methane diffuse than sulfur dioxide?

molar mass of CH₄ is 16.0 g/mol

molar mass of SO₂ is 64.0 g/mol

What do you expect?

CH₄ to be faster,
but how much faster?

Ratio of molar masses = 16/64 = 1/4

Ratio of sqrt (molar mass of the gas) = 1/2

Ratio of velocity = 1 / (1/2) = 2



velocity - u

For any two gases A and B:

$$\frac{u_A}{u_B} = \sqrt{\frac{\text{molar mass of B}}{\text{molar mass of A}}}$$

$$\left(\frac{u_A}{u_B}\right)^2 = \left(\sqrt{\frac{\text{molar mass of B}}{\text{molar mass of A}}}\right)^2$$

$$\left(\frac{u_A}{u_B}\right)^2 = \frac{\text{molar mass of B}}{\text{molar mass of A}}$$

$$\begin{aligned} (\text{molar mass of A})(u_A)^2 &= \\ &= (\text{molar mass of B})(u_B)^2 \end{aligned}$$

KE of any gas is equal at given temperature

KE of any gas is proportional to temperature

IDEAL GAS - ASSUMPTIONS

Any gas will be considered as an ideal gas if these four assumptions are made:

KE of any gas is proportional to temperature

Graham's law as discussed on the previous slide

Gas particles have no volume

Dalton's law – it doesn't matter what gas we have

@ SATP: 1 mole of liquid water (18.0 g) occupies 18 mL
(0.018 L approximate volume of all particles)

@ SATP: 1 mole of gas water (18.0 g) occupies 24.8 L

1 mole of H₂O gas occupies a volume of
(24.8 – 0.018) = 23.782 L which is 1378 !!!
time more than a volume of liquid H₂O

Gas particles do not attract each other

Dalton's Law

Pressure would depend upon nature of molecules

All collisions must be perfectly elastic

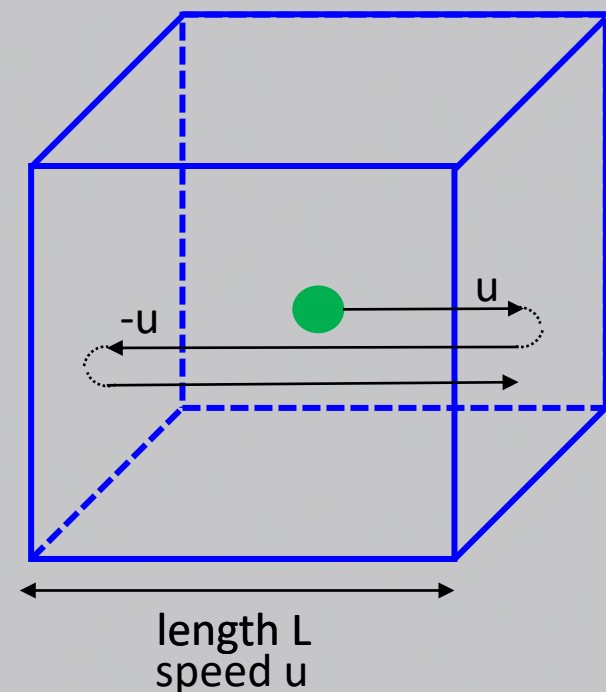
Graham's Law

If they weren't, the KE would change



KINETIC MODEL OF GASES

gas molecule in a box moving in 1D:



one molecule of gas moves between walls of the container (distance L) with speed u



The walls of the box experience the force when the gas molecule bounces back and forth:

Force = $m \times a$

$a = \Delta u / \Delta t$

m – mass
a - acceleration

Force = $m \times \Delta u / \Delta t$

Force = $\Delta \text{mu} / \Delta t$

↓
momentum

Force = $\Delta \text{momentum} / \Delta t$

→ momentum = $m \times u = mu$

← momentum = $m \times (-u) = -mu$

change in momentum = $fin - in = -mu - mu = -2mu$

for a given particle of gas

change in momentum = $fin - in = mu - (-mu) = 2mu$

on wall of container

Force = $2 mu / \Delta t$

let's explore Δt further...

KINETIC MODEL OF GASES

$$\text{Force} = 2 mu / \Delta t$$

gas particle travels distance L between collisions with the speed u :

because $u = L / t$, time $t = L / u$, so:

$$\text{Force} = 2 mu / (L/u)$$

for a gas particle in a box which travels distance L in 1D with the speed u , the force exerted on the wall of the box is given by:

$$\text{Force} = 2 mu^2 / L$$



KINETIC MODEL OF GASES

in 1D: $\text{Force} = 2 mu^2 / L$

gas molecule in a box moving in 3D:

in 3D: $\text{Force} = 2 mu_x^2 / L + 2 mu_y^2 / L + 2 mu_z^2 / L$

$$\text{Force} = 2 m(u_x^2 + u_y^2 + u_z^2) / L$$

$$U = u_x^2 + u_y^2 + u_z^2$$

$\text{Force} = 2 mU^2 / L$

but because we are interested in pressure:

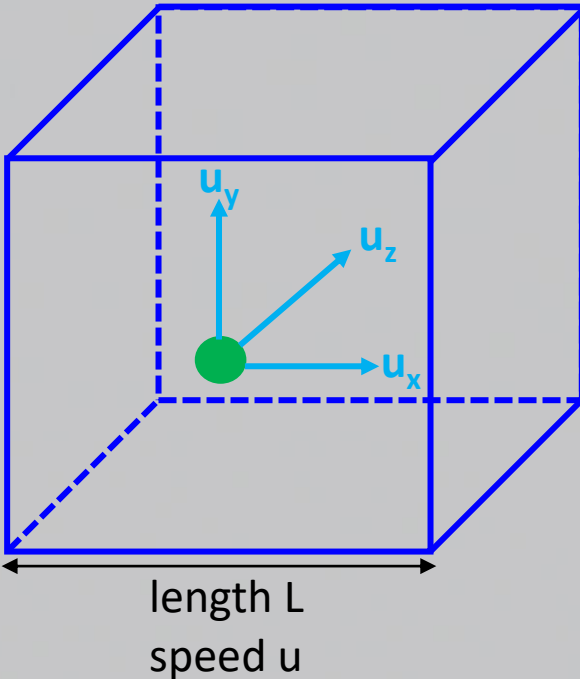
$$\text{Pressure} = \text{Force} / \text{area}$$

$$\text{area} = 6 \text{ faces} = 6 \times L^2$$

$$\text{Pressure} = 2 mU^2 / L \div 6 L^2$$

$$\text{Pressure} = mU^2 / 3L^3$$

$$\text{Pressure} = mU^2 / 3V$$



KINETIC MODEL OF GASES

so far considered for only one molecule

$$\text{Pressure} = mU^2 / 3V$$

if more molecules present = $n \times N_A$

$$\text{Pressure} = (n \times N_A) mU^2 / 3V$$

$$\text{Pressure} = (n \times N_A) \times 2 \times \left(\frac{1}{2} mU^2 \right) / 3V$$

$$\text{Pressure} = (n) \times 2 \times (KE) / 3V$$

From Graham's law – $KE = \text{const} \times T$

$$\text{Pressure} = (n) \times 2 \times (\text{constant} \times T) / 3V$$

$$\text{Pressure} = (\text{CONSTANT}) nT / V$$



$$PV = nRT$$

ROOT MEAN SQUARE SPEED

$$\text{Pressure} = (n) \times 2 \times (\text{KE}) / 3V$$

$$PV/n = 2/3 \times (\text{KE}) = RT$$

$$\text{KE per mole} = N_A (1/2 mU^2)$$

$$U^2 = 3RT / N_A (m) \quad \text{MM}$$

U^2 = average of the squares of the velocity

$$u_{\text{rms}} = \text{sqrt } U^2$$

rms = Root Mean Square

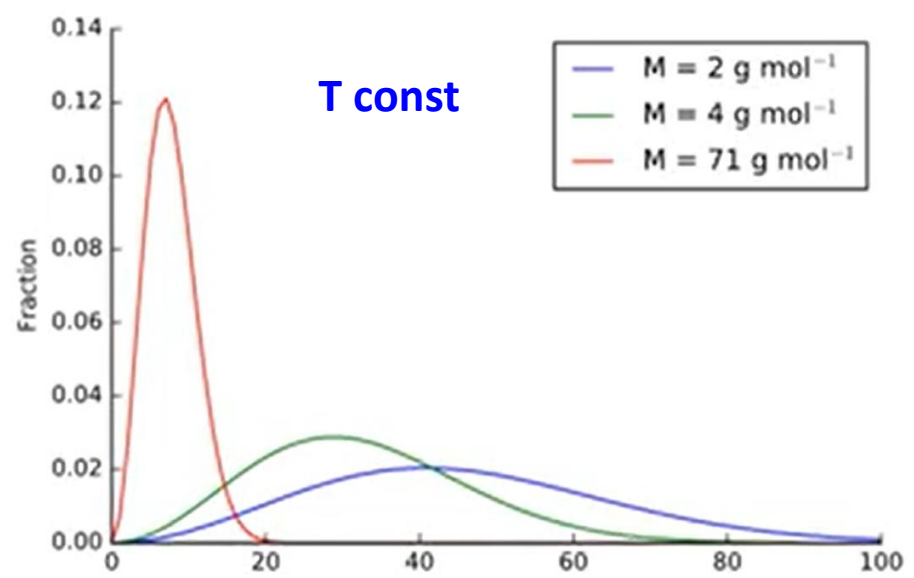
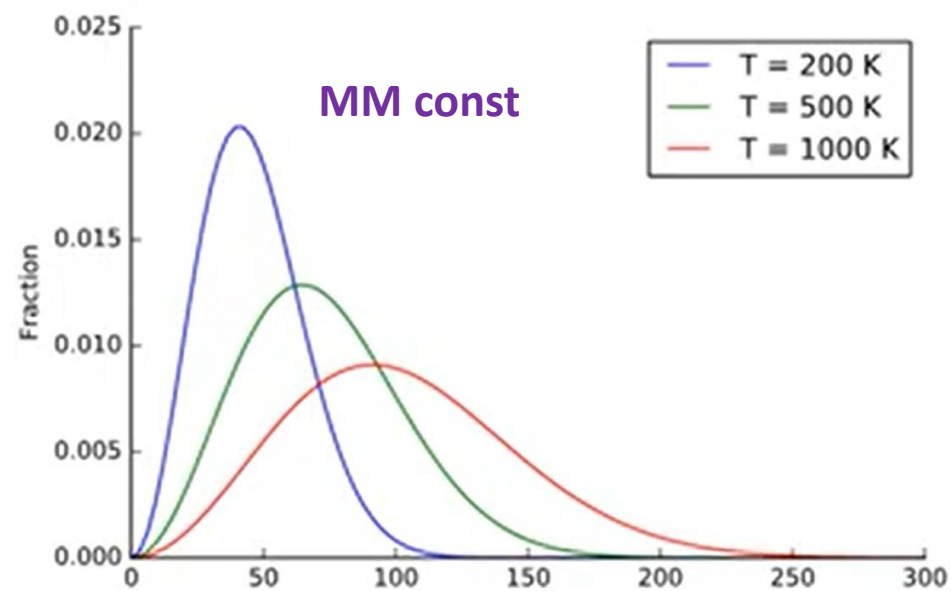
$$u_{\text{rms}} = \sqrt{\frac{3RT}{MM}}$$

root mean square speed

The root-mean-square speed is the measure of the speed of particles in a gas, defined as the square root of the average velocity-squared of the molecules in a gas.



KINETIC MOLECULAR THEORY

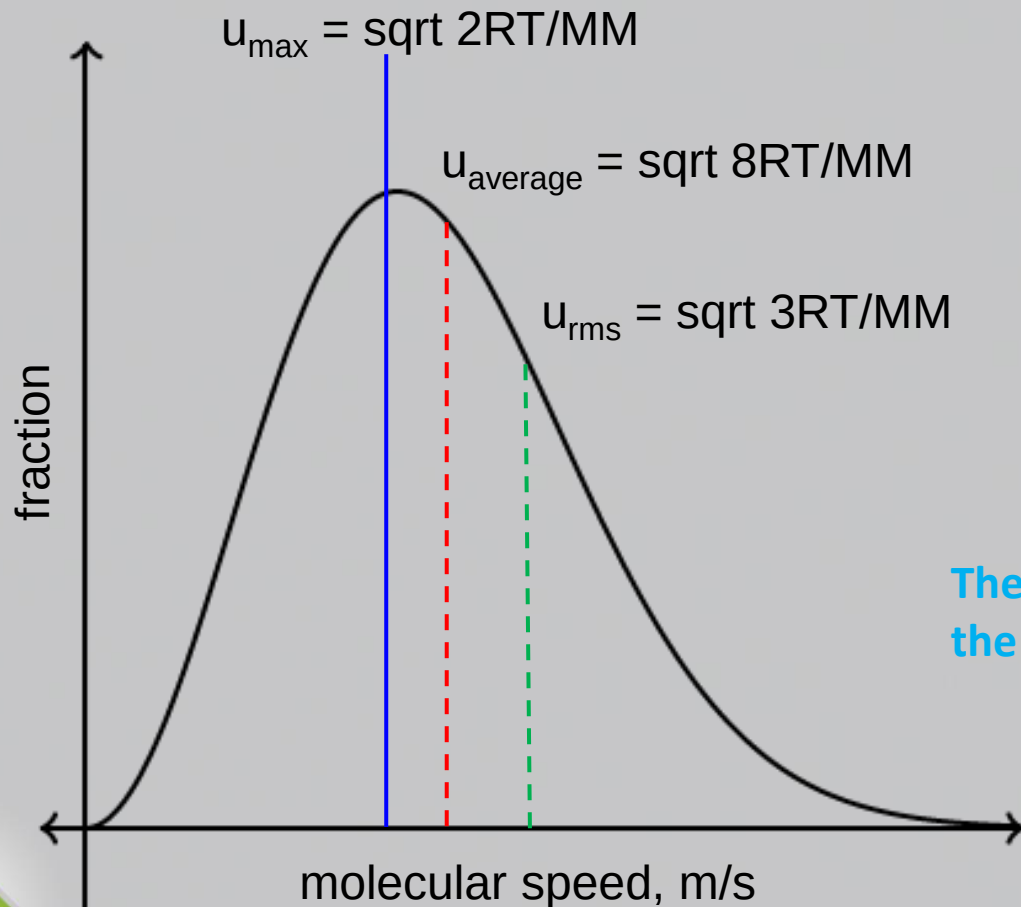


Gas	u m s ⁻¹ (20 degC)
H ₂	1912
He	1352
NH ₃	656
H ₂ O	637
N ₂	511
O ₂	478
Ar	427
CO ₂	407
C ₄ H ₁₀	355
Cl ₂	320
SO ₃	302
Br ₂	213

MAXWELL BOLTZMAN DISTRIBUTION OF SPEED

distribution of molecular speeds – the fraction of gas molecules moving at each speed at any instant

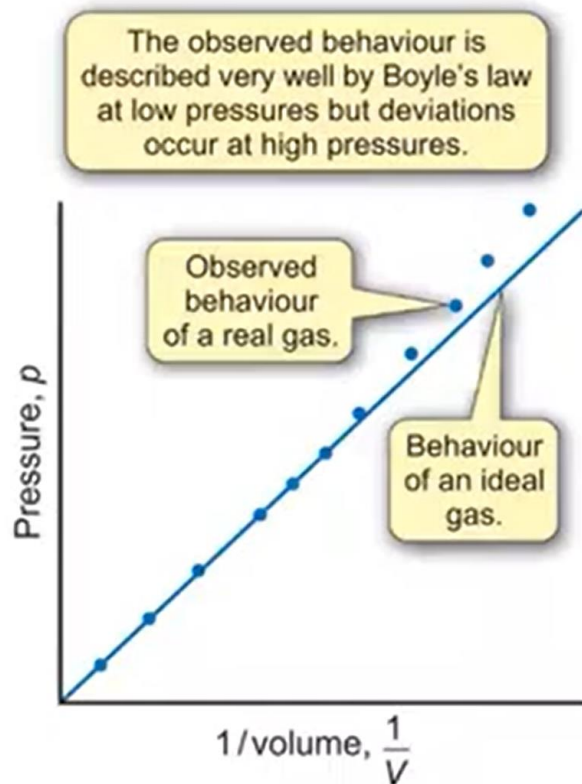
example: N_2 @ 300 degC



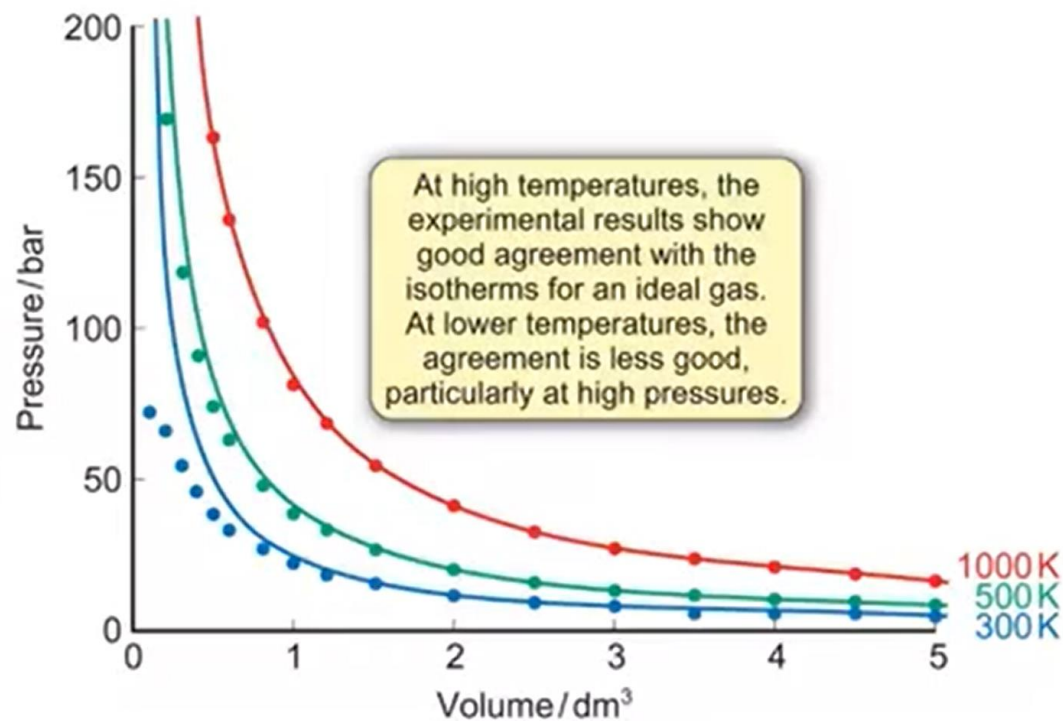
The u values are different because the curve is not symmetric.



REAL GAS CORRECTIONS



Chem³, p. 372



DEVIATIONS WITH:

High pressure

Low temperature

Low volume



REAL GAS CORRECTIONS

Van der Waals Equation:

Gas particles have no volume

$$\text{actual } V = V_{\text{container}} - nb$$

b depends on gas

Gas particles do not attract or repel each other

$$\text{actual } P = P_{\text{observed}} + (n/V)^2a$$

a depends on gas

The attractions and repulsions between molecules are called intermolecular forces

$$PV = nRT$$

$$(P_{\text{observed}} + (n/V)^2a) (V_{\text{container}} - nb) = nRT$$

REAL GAS EQUATION



SAMPLE PROBLEM

Helium and methane, CH_4 , are both found in natural gas and can be separated by diffusion. What is the ratio of the diffusion rates for the two species (rate of diffusion for He divided by the rate for CH_4)?

- a) 16.06
- b) 0.499
- c) 2.00
- d) 4.01
- e) 0.249

Consider two 1-L samples of gas, one H_2 and one O_2 , both at 1 atm and 25°C . Compare the samples in terms of the characteristics listed.

time for a given fraction of O_2 molecules to effuse ____ time for a given fraction of H_2 molecules to effuse

- a) is unrelated to
- b) is greater than
- c) is equal to
- d) None of these
- e) is less than

At a particular pressure and temperature, it takes 4.55 min for a 1.5-L sample of He to effuse through a porous membrane. How long does it take for 1.5 L of F_2 to effuse under the same conditions?

- a) 0.324 min
- b) 1.48 min
- c) 3.081 min
- d) None of these is within 5% of the correct answer.
- e) 14.0 min