

CHEMISTRY
XL-14A
GASES



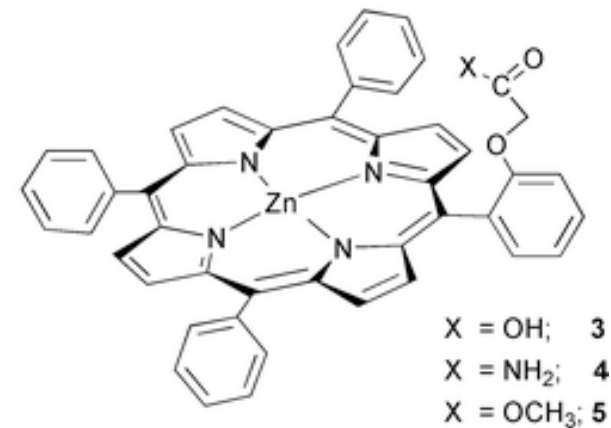
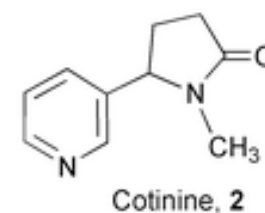
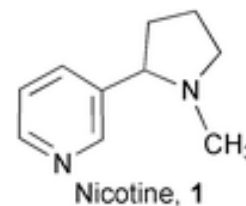
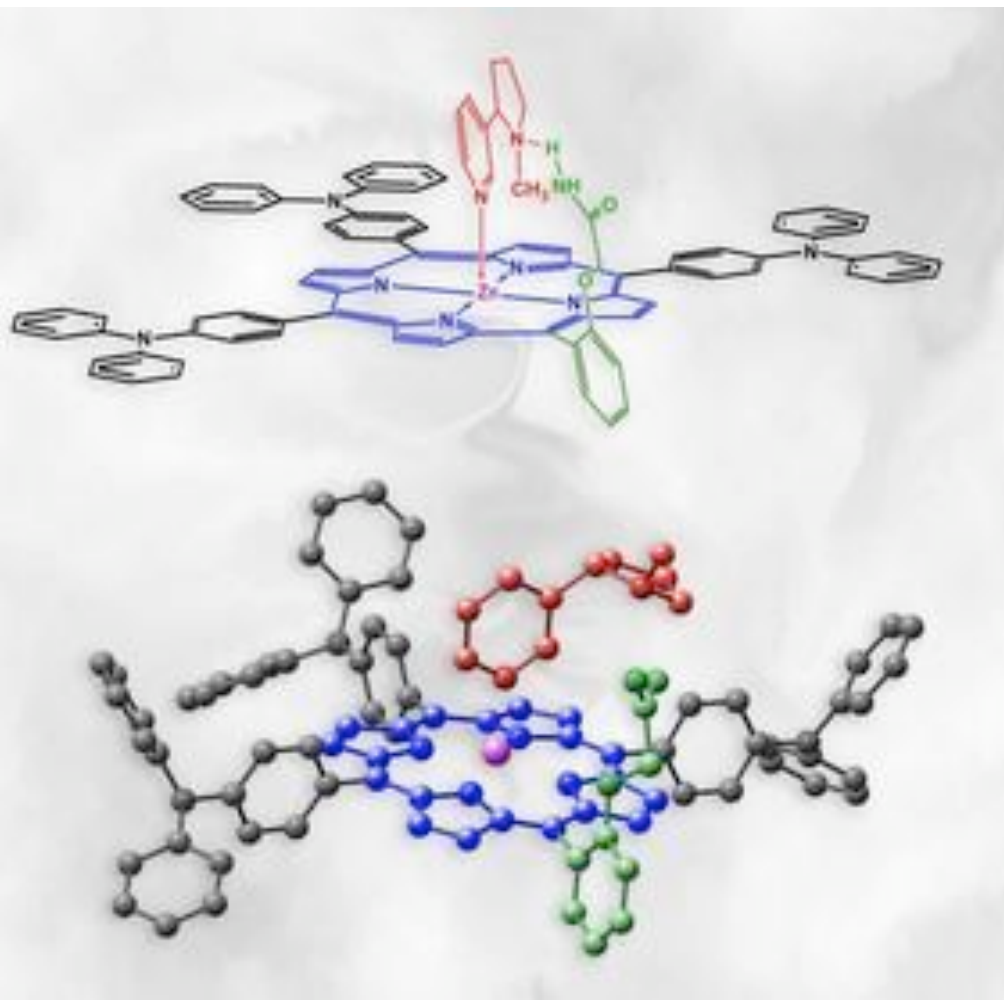
August 6, 2011

Robert Iafe

Chemistry in the News

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□



meso-tetraphenylporphyrinatozinc
(TPP)Zn

Coordination Compounds

3

- $\text{Na}_2[\text{PtCl}_2(\text{ox})_2]$ sodium dichloridobis(oxalato)platinate(IV)
 - Overall complex charge = -2
 - Ligand charge = Cl^{-1} and oxalato $\text{C}_2\text{O}_4^{2-}$
 - Metal charge + ligand charge = overall complex charge
 - $\text{Pt} + (-6) = -2$
 - $\text{Pt} = +4$

- $[\text{CoBr}(\text{NH}_3)_5]\text{SO}_4$ pentaamminebromidocobalt(III) sulfate
 - Overall complex charge = -2
 - Ligand charge = Br^{-1} and NH_3
 - Metal charge + ligand charge = overall complex charge
 - $\text{Co} + (-1) = +2$
 - $\text{Co} = +3$

Overview

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- The Nature of Gases
- The Gas Laws
- Molecular Motion
- Real Gases

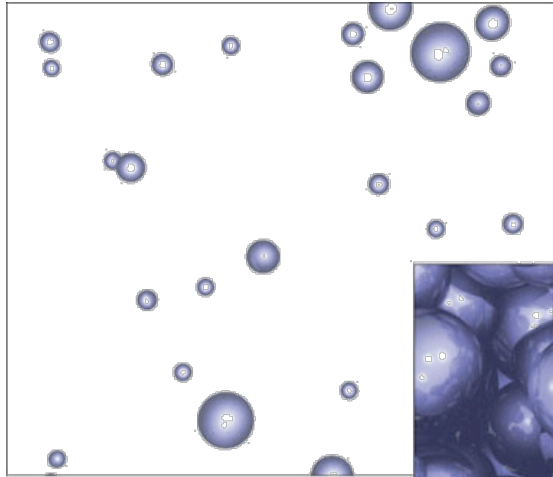
The Nature of Gases

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- Properties of Gases
- Pressure
- Measuring Pressure
 - Manometers
 - Barometers
- Units of Pressure

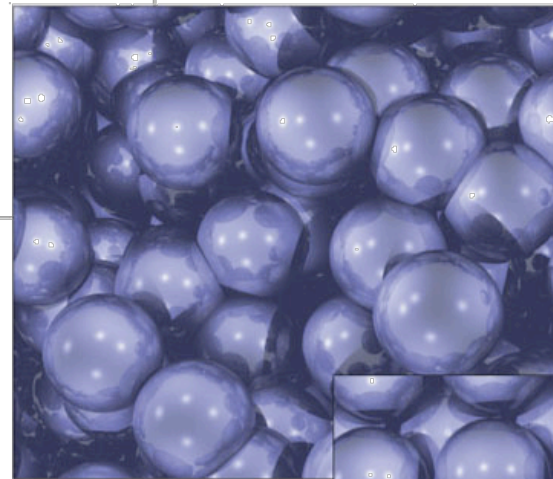
The States of Matter

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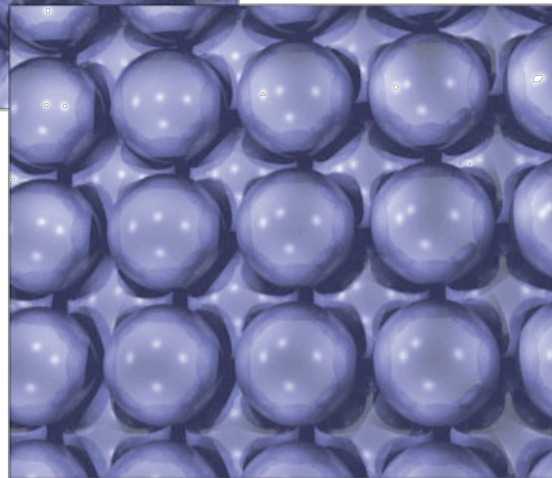
(a)

Gas



(b)

Liquid



Solid

Differences between Gases and Condensed (Liquid, Solid) Phases

7

Gases	Liquids, Solids
Molar Volume - Large - 24,000 cm ³ /mol	Molar Volume – Small 10-100 cm ³ /mol
Distance between particles Large - 30 x 10 ⁻¹⁰ m separation	Distance between particles - Slightly larger than bond lengths - 3-5 x 10 ⁻¹⁰ m separation
Interatomic (intermolecular) forces play very small role in behavior	Behavior strongly influenced by long-range and short range forces

The Gaseous State

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- Macroscopic Properties (mass density)
 - Temperature, Pressure and Volume
 - Ideal Gas Law
- Microscopic Properties (number density)
 - Molecular Motions (Kinetic Theory)
 - Collisions between molecules
- Real Gases
 - Intermolecular forces
 - van der Waals equation

The Chemical Composition of Air

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Constituent	Formula	Fraction by Volume
Nitrogen	N ₂	0.7808
Oxygen	O ₂	0.2095
Argon	Ar	0.00934
Carbon Dioxide	CO ₂	0.00038
Other Constituents:		0.9995

Neon, Helium, Methane, Krypton, Hydrogen, Dinitrogen monoxide, Xenon, Water, Ozone, Carbon Monoxide, Nitrogen Dioxide, Sulfur Dioxide

Pressure of Gases

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Pressure – force exerted by gas on its surroundings

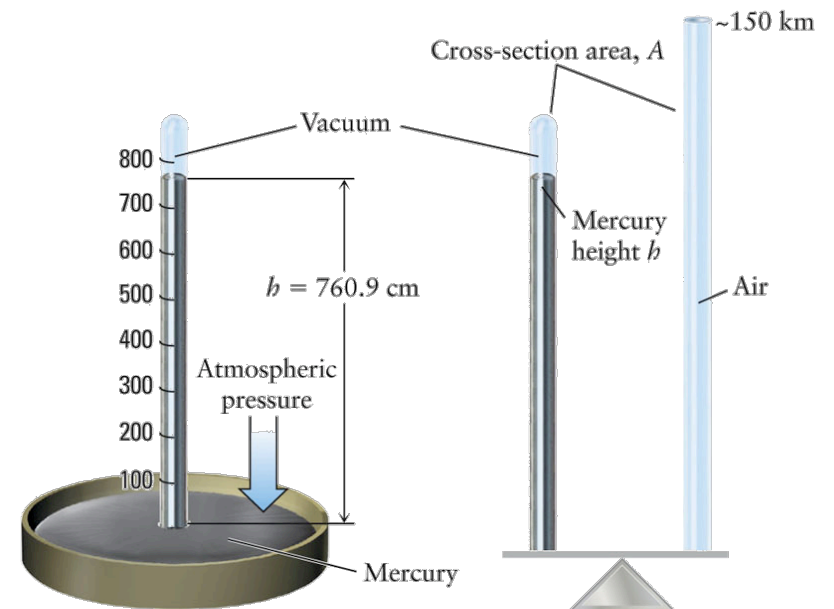
What are ‘Surroundings’?

Everything except the gas

Surroundings in this room – walls, floor, ceiling, people, chairs, etc...

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}}$$

$$P = \frac{F}{A}$$



(a)

(b)

Pressure of Gases

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Pressure – force exerted by gas on its surroundings

What are ‘Surroundings’?

Everything except the gas

Surroundings in this room – walls, floor, ceiling, people, chairs, etc...

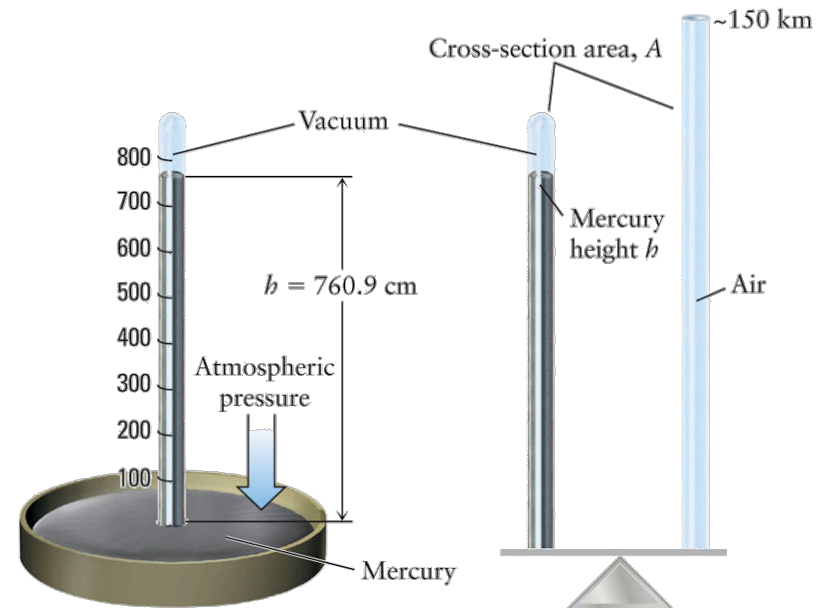
Evangelista Torricelli (1608 – 1647)

Glass tube filled with mercury (Hg)

Turned upside down into dish of Hg

Mercury fell, leaving a vacuum

Height of Hg ~ 760 mm
(varies by day and location)



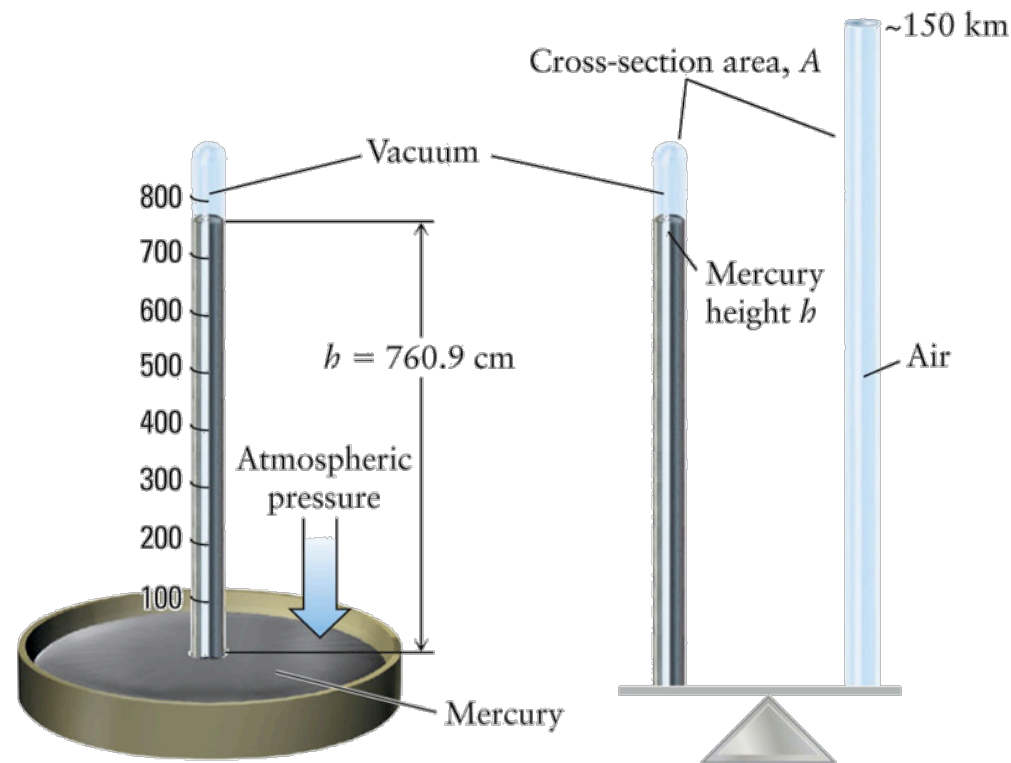
(a)

(b)

Measuring Pressure - Barometer

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Balance between liquid Hg tube and a 2nd tube of the same area and the height of Earth's atmosphere.



Height of the Hg varies as it balances the atmospheric pressure

How the Barometer works: Physical definition of Pressure

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$$P = \frac{F}{A} \quad F = mg$$

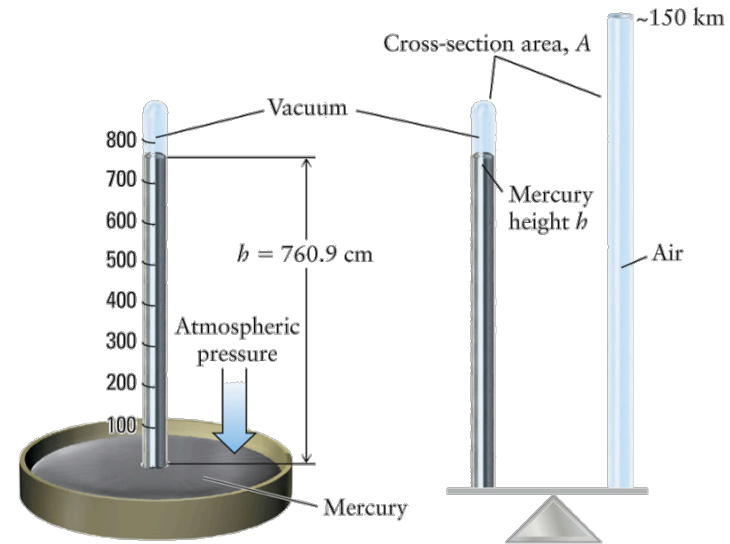
Force = mass × acceleration

$$P = \frac{F}{A} = \frac{mg}{A}$$

Volume = Area × height

$$V = Ah \quad A = \frac{V}{h}$$

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



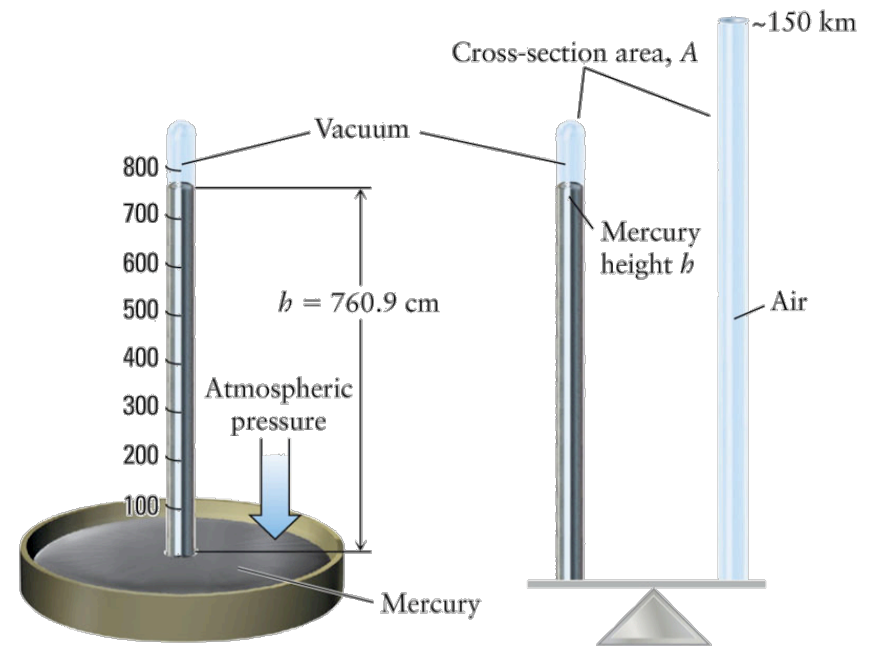
How the Barometer works: Physical definition of Pressure

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

$$\text{Density} = \frac{\text{mass}}{\text{Volume}} \quad \rho = \frac{m}{V}$$

$$P = \rho gh$$



How the Barometer works: Physical definition of Pressure

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$$P = \rho g h$$

$$\rho (\text{Hg}) = 13.5951 \text{ g/cm}^3$$

$$g = 9.80665 \text{ m/s}^2$$

$$h = 760 \text{ mm}$$

Calculate the atmospheric pressure in Pascals ($1 \text{ Pa} = 1 \text{ kg/ms}^2$):

The Manometer

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Manometer – U-shaped tube connected to experimental system

For an open-tube manometer:

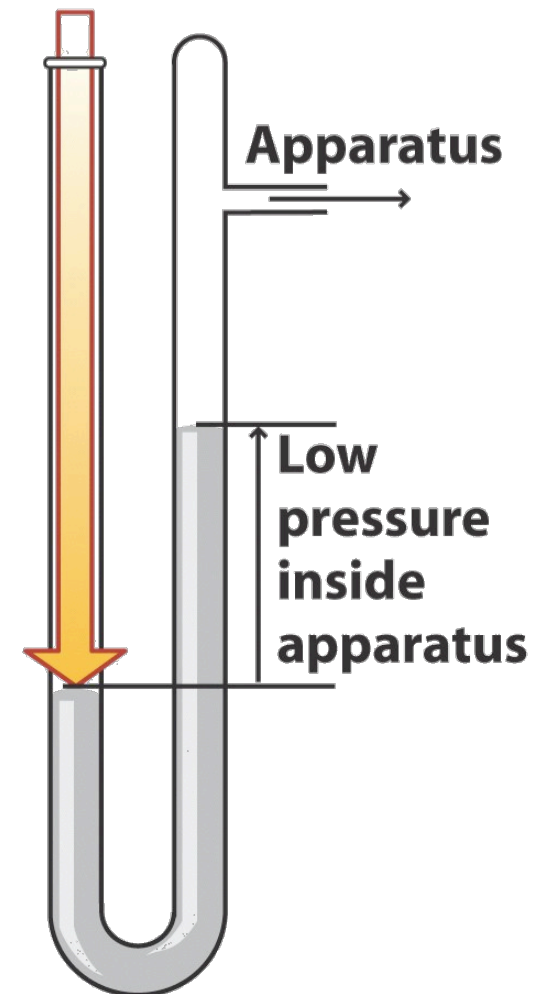
Open side higher than closed side:

$$P_{\text{sys}} = P_{\text{atm}} + P_h$$

Open side lower than closed side:

$$P_{\text{sys}} = P_{\text{atm}} - P_h$$

$$P_h = \rho gh$$



Units of Pressure

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T A B L E 9.2 Units of Pressure

Unit	Definition or Relationship
pascal (Pa)	$1 \text{ kg m}^{-1} \text{ s}^{-2}$
bar	$1 \times 10^5 \text{ Pa}$
atmosphere (atm)	101,325 Pa
torr	1/760 atm
760 mm Hg (at 0°C)	1 atm
14.6960 pounds per square inch (psi, lb in ⁻²)	1 atm

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$$1 \text{ atm} = 1.01325 \text{ bar} = 760 \text{ mm Hg} = 101,325 \text{ Pa}$$

Standard Pressure (1 bar)

$$1 \text{ mm Hg} = 1 \text{ Torr}$$

The Gas Laws

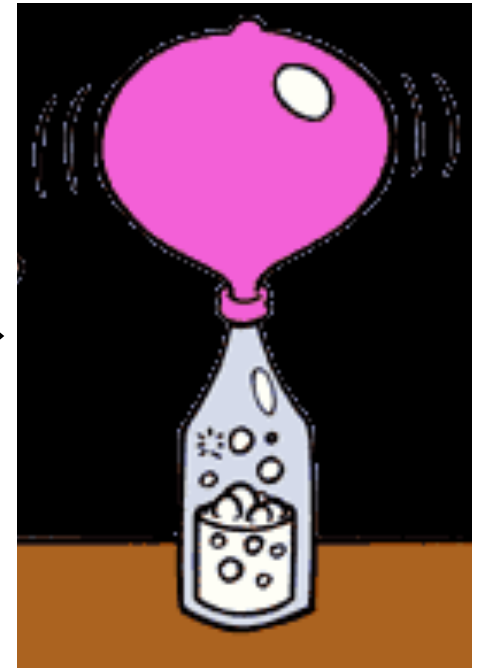
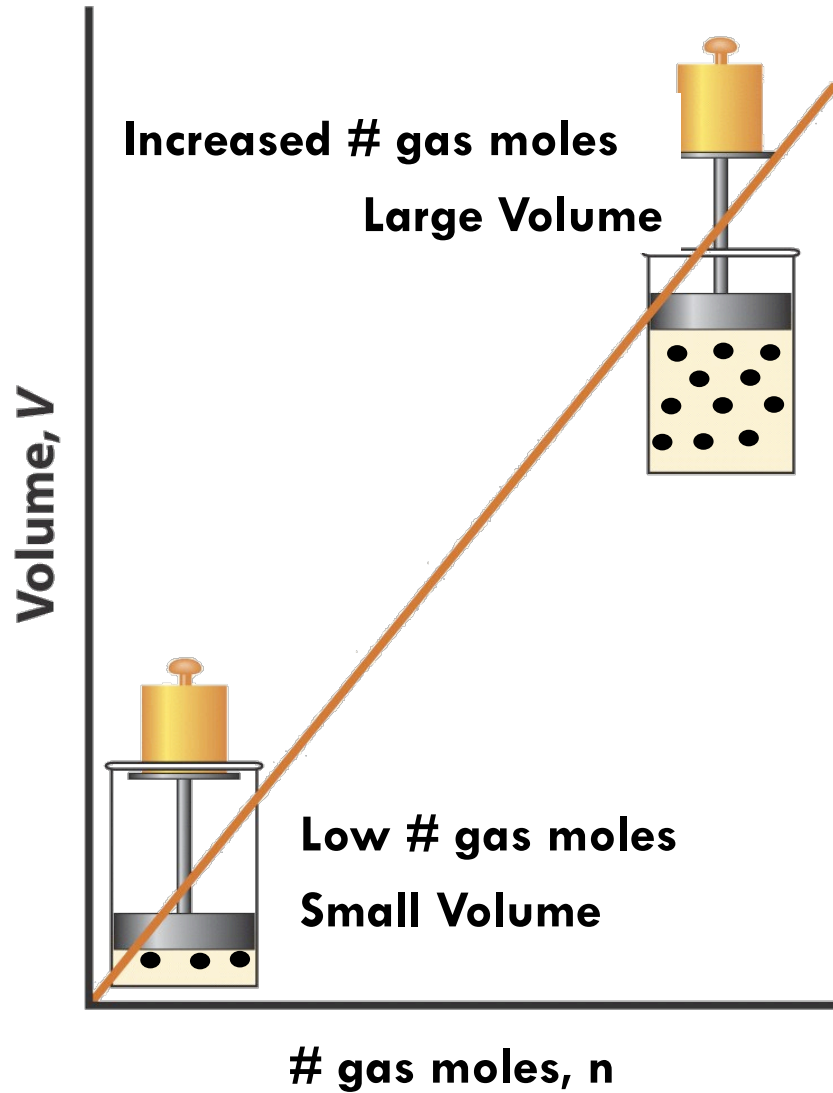
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- Avogadro's Law
- Boyle's Law
- Charles' Law
- Ideal Gas Law
- Gas Density
- Stoichiometry with Gases
- Mixtures of Gases

Avogadro's Law

$$V \propto n$$

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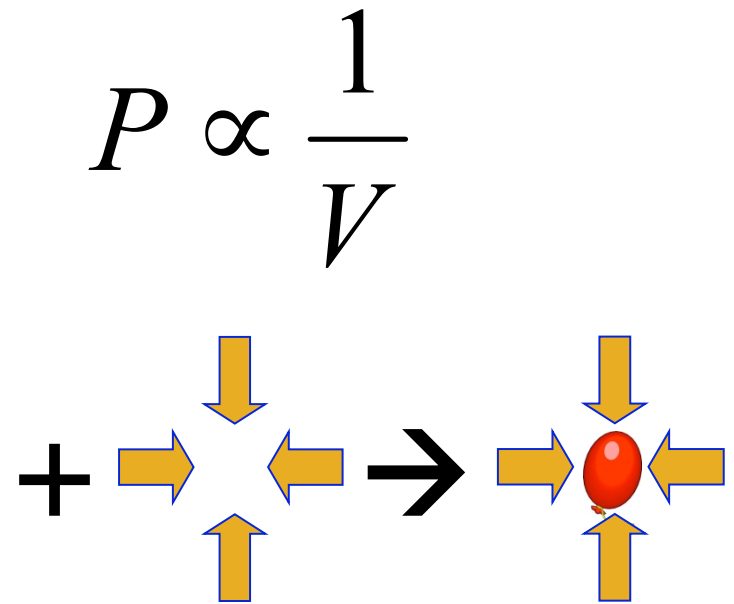
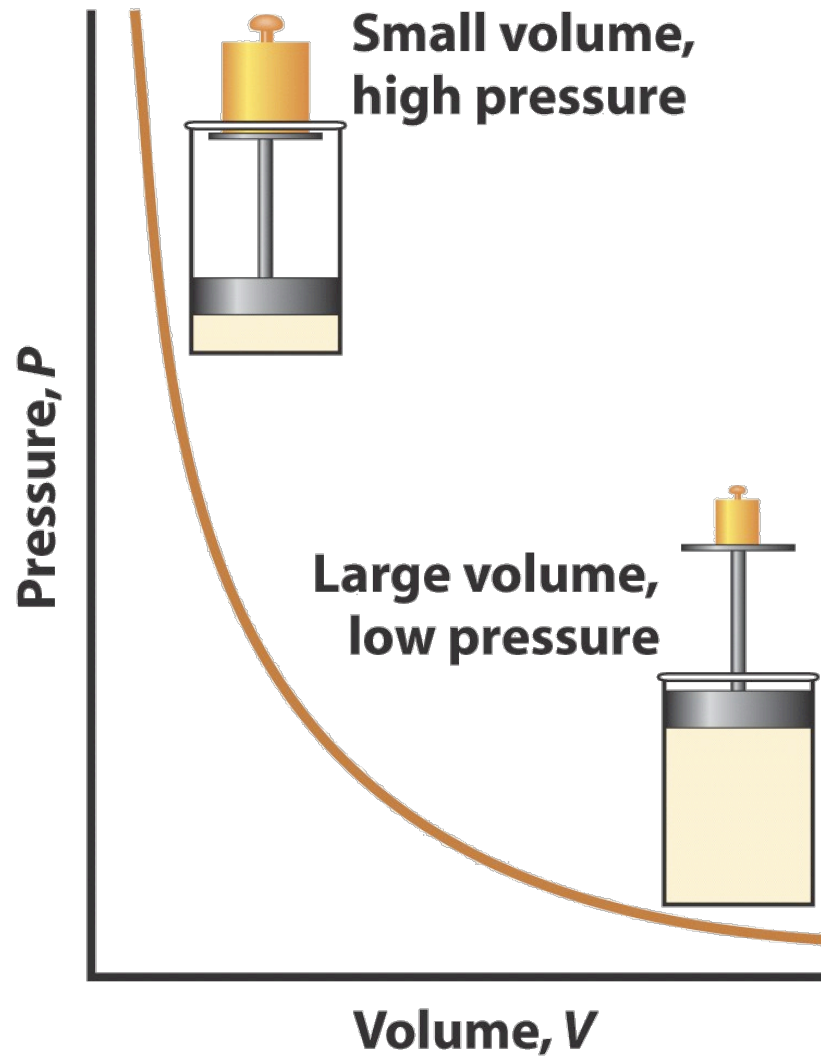
$$\frac{n_1}{V_1} = \frac{n_2}{V_2}$$

Constant

P, T

Boyle's Law

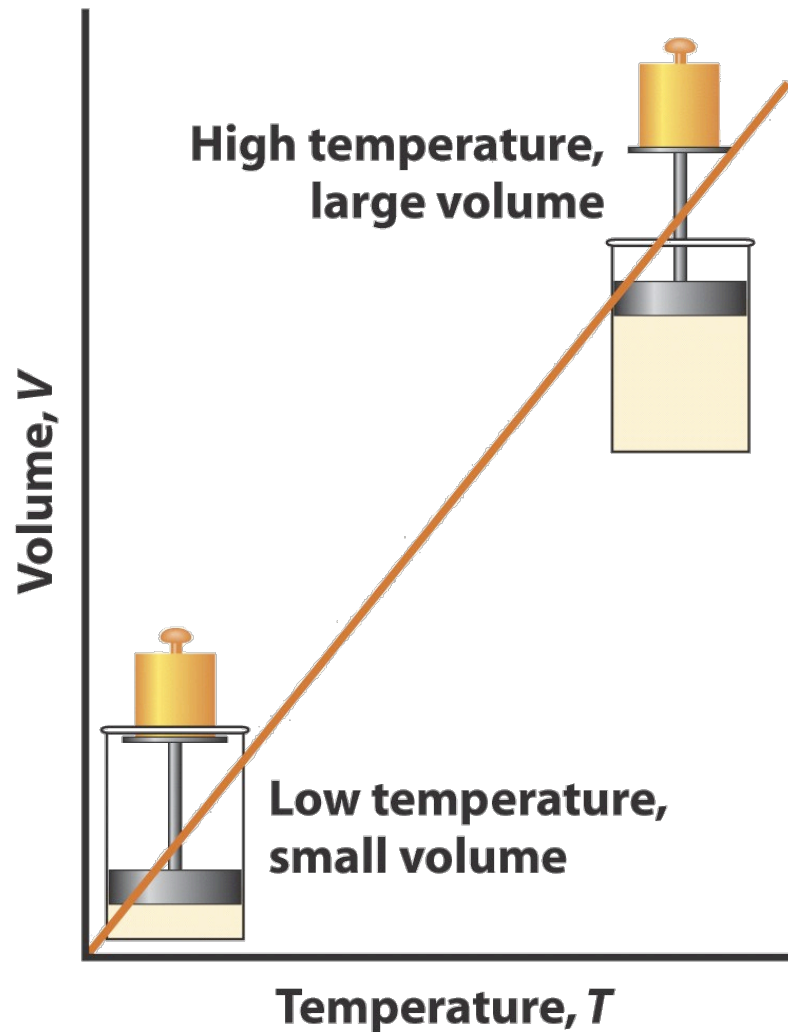
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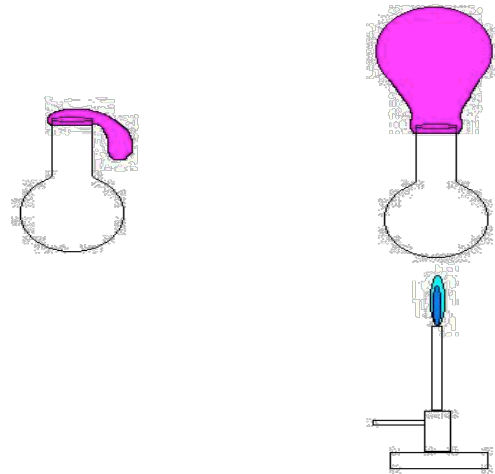
$$P_1 V_1 = P_2 V_2$$

Charles' Law

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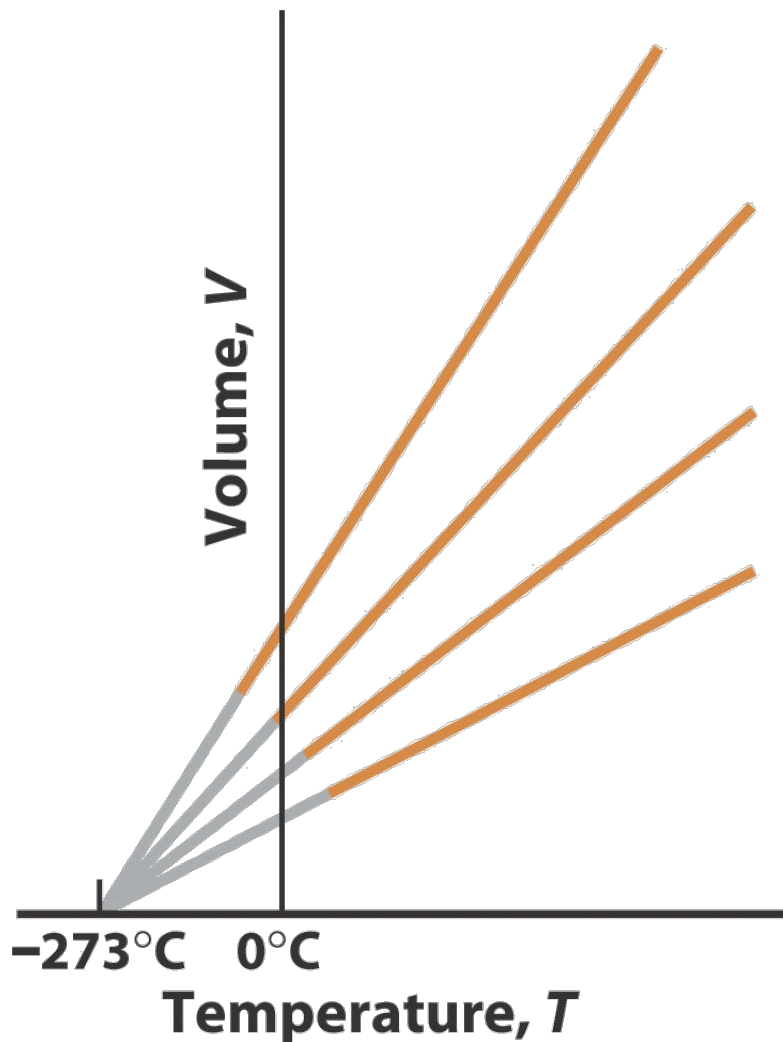
$$V \propto T$$



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

Charles' Law and Temperature

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$$V = V_0 \left(1 + \frac{T}{273.15^\circ\text{C}} \right)$$

T (units of °C)

$$^\circ\text{F} = \frac{9}{5}^\circ\text{C} + 32$$

T = -273.15 C?

Must be the lowest possible T!

T = 0 K Absolute Zero

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

Gay-Lussac's and Avogadro's Laws

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Boyle's Law Pressure and Volume	$PV = \text{Constant}$	Constant T, n
Charles's Law Temp and Volume	$\frac{V}{T} = \text{Constant}$	Constant P, n
Avogadro's Law moles and Volume	$\frac{n}{V} = \text{Constant}$	Constant T, P
Gay-Lussac's Law Pressure and Temp	$\frac{P}{T} = \text{Constant}$	Constant V, n

Gas Law Practice

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1. Two 100 mL round bottom flasks are connected by a stopcock. With the stopcock closed, nitrogen gas at 2.00 atm is contained in one of the flasks. Calculate the pressure of the gas when the stopcock is opened.
2. Oxygen is contained in a flexible balloon. At room temperature (23 °C), the balloon is 0.50 L in volume. Calculate the size of the balloon on a hot day (38 °C).
3. Methane gas is sealed in a 250 mL E-flask at room temperature. It exerts 1.15 atm of pressure at this temperature. What is the pressure of the methane at 110 °C?

Deriving the Ideal Gas Law

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$$V \propto n$$

Avogadro's Law

$$V \propto \frac{1}{P}$$

Boyle's Law

$$V \propto T$$

Charles's Law



$$V \propto \frac{nT}{P}$$

Ideal Gas Law

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$$V \propto \frac{nT}{P} \longrightarrow V = R \frac{nT}{P}$$

Therefore:

$$PV = nRT$$

R = Universal Gas Constant

$$R = 0.082058 \text{ L atm/ mol K}$$

$$R = 8.314472 \text{ J/mol K}$$

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

More about the Ideal Gas Law:

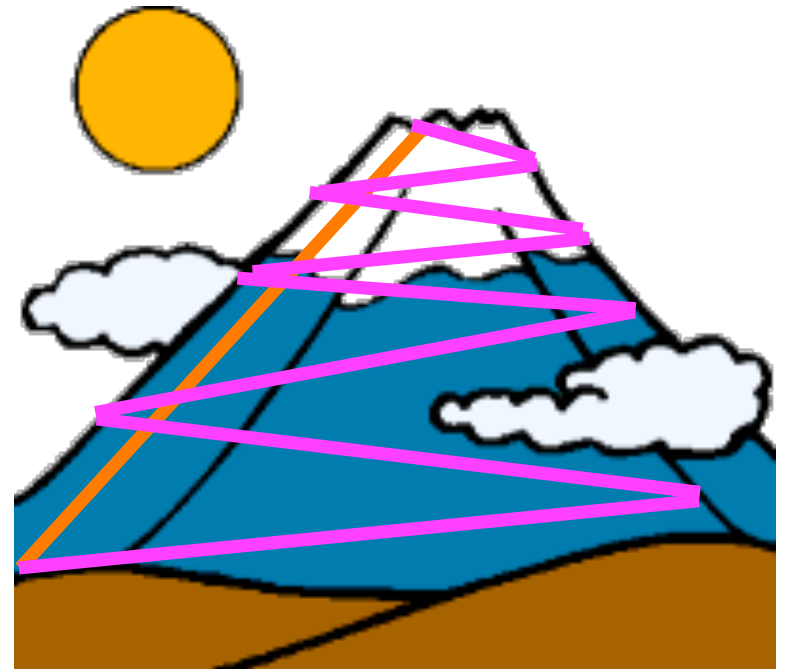
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Ideal gas law is a **State Equation** – which relates State Functions

State Function – property of a system determined by the current state of the system

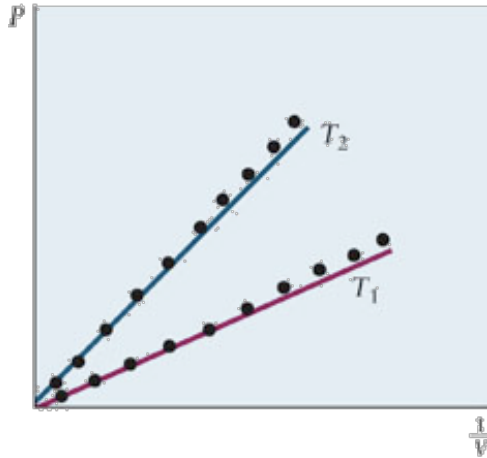
Pressure Volume Temperature Altitude
Energy

Path Function – properties determined by the path taken work heat miles hiked

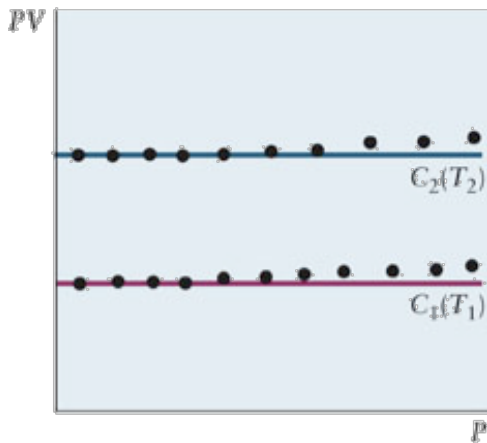


Ideal Gas Law: Approximations

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(b)



(c)

$$PV = nRT$$

What is an 'Ideal Gas'?

- Low P , High T
- Gas particles have $V = 0$
- Non-interacting gas particles
- Collisions with walls are perfectly elastic
(KE of gas particles is conserved)

Ideal Gas Law Practice

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- What volume will 2.00 g of hydrogen gas take up at STP?

(STP = standard temperature and pressure, 1 atm and 0 °C)

Ideal Gases: Molar Volume

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Gases have high Molar Volumes (V_m):

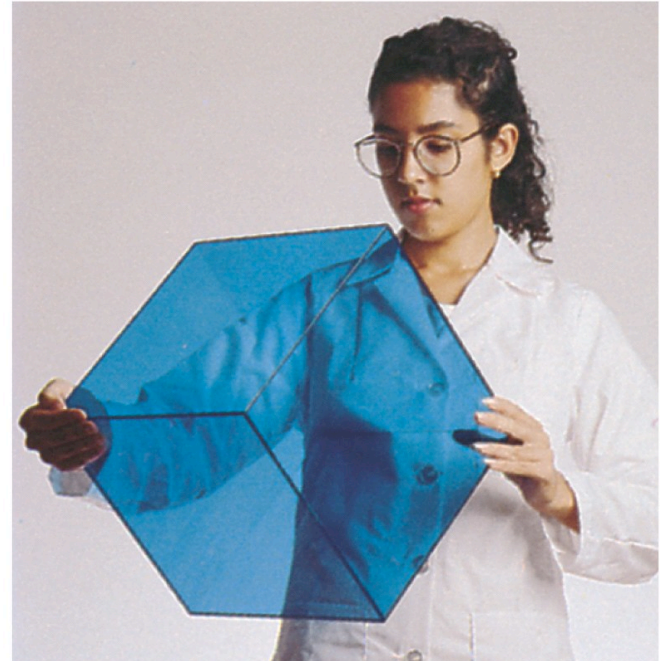
$$V_m = \frac{V}{n} = \frac{nRT / P}{n} = \frac{RT}{p}$$

STP (standard T and P) →

$$V_m = 22.41 \text{ L/mol}$$

SATP (standard ambient T and P) →

$$V_m = 24.79 \text{ L/mol}$$



Ideal gas	22.41
Argon	22.09
Carbon dioxide	22.26
Nitrogen	22.40
Oxygen	22.40
Hydrogen	22.43

Ideal Gases: Gas Density

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Molar Concentration – # moles per unit Volume

can be applied to any fluid phase

$$\frac{n}{V} = \frac{PV/RT}{V} = \frac{P}{RT}$$

Density – # grams per unit Volume

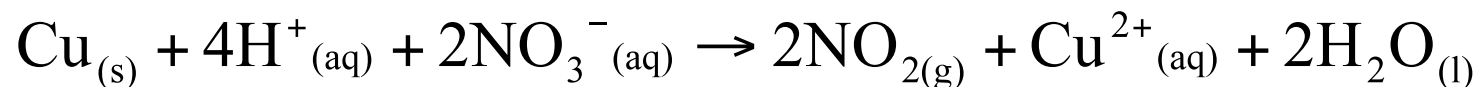
$$\rho = \frac{m}{V} = \frac{nM}{V} = \frac{(PV/RT)M}{V} = \frac{MP}{RT}$$

Gas is compressed \rightarrow both molar concentration & density increases

Chemical Calculations for Gases: Ideal Gas Law & Stoichiometry

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Practice Problem:



6.80 g $\text{Cu}_{(s)}$ is consumed.

$\text{NO}_{2(g)}$ is collected at $P = 0.970 \text{ atm}$, $T = 45 \text{ }^\circ\text{C}$.

Calculate the volume of $\text{NO}_{2(g)}$ produced:

Solution:

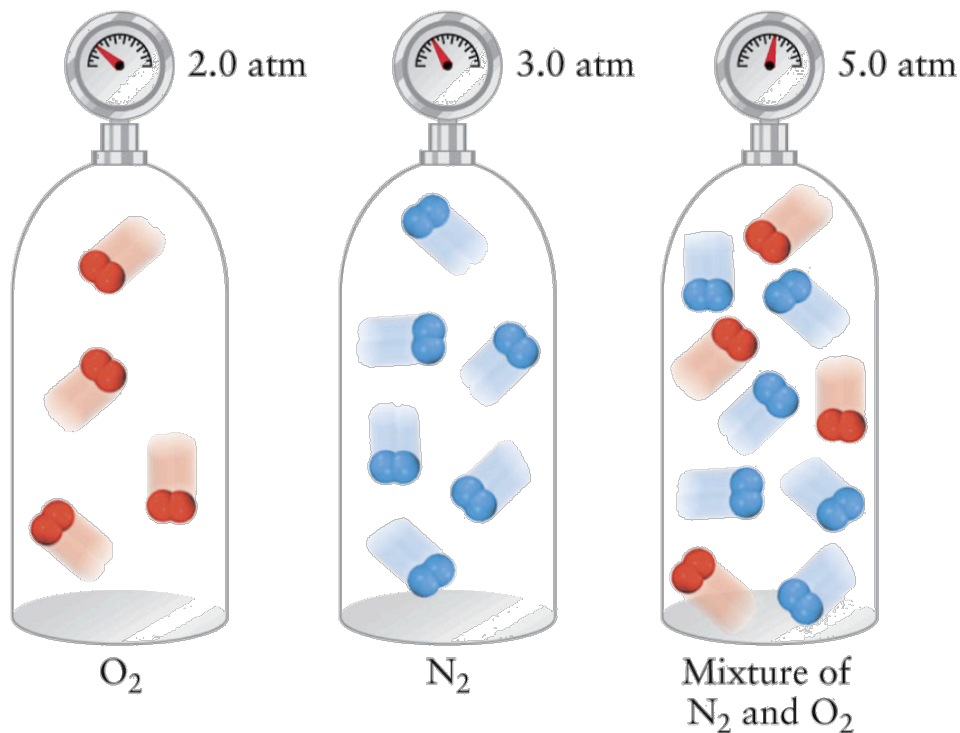
$$V(\text{NO}_{2(g)}) = 5.76 \text{ L}$$



Mixtures of Gases

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Partial Pressure of a single gas component: pressure it would exert if it were the only gas component present



John Dalton:

P_{tot} = sum of partial pressures of component gases

Dalton's Law

$$P_{\text{tot}} = P_A + P_B + P_C + \dots$$

$$P_{\text{tot}} = P_{N_2} + P_{O_2}$$

Mixtures of Gases

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$$P_A = n_A \frac{RT}{V}$$

$$P_{tot} = P_A + P_B + P_C + \dots$$

$$P_{tot} = P_A + P_B + P_C + \dots = (n_A + n_B + n_C + \dots) \frac{RT}{V} = n_{tot} \frac{RT}{V}$$

$$P_A = n_A \frac{RT}{V} \bigg/ P_{tot} = n_{tot} \frac{RT}{V} \longrightarrow \frac{P_A}{P_{tot}} = \frac{n_A}{n_{tot}} \quad P_A = \frac{n_A}{n_{tot}} P_{tot}$$

$$P_A = X_A P_{tot} \quad X_A = \frac{n_A}{n_{tot}} \quad X_A = \text{Mole fraction of gas A}$$

Mixtures of Gases

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The atmospheric pressure at the surface of Venus is 90.8 atm.

The Venusian atmosphere is 96.5 % CO₂ and 3.5 % N₂ by Volume.

Compute the mole fraction and partial pressure of N₂ in the Venusian atmosphere.

$$P_A = X_A P_{tot} \quad X_A = \frac{n_A}{n_{tot}} \quad X_A = \frac{\text{Mole fraction}}{\text{of gas A}}$$

Molecular Motion

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- Diffusion and Effusion
- Kinetic Model of Gases
- Maxwell Distribution of Speeds

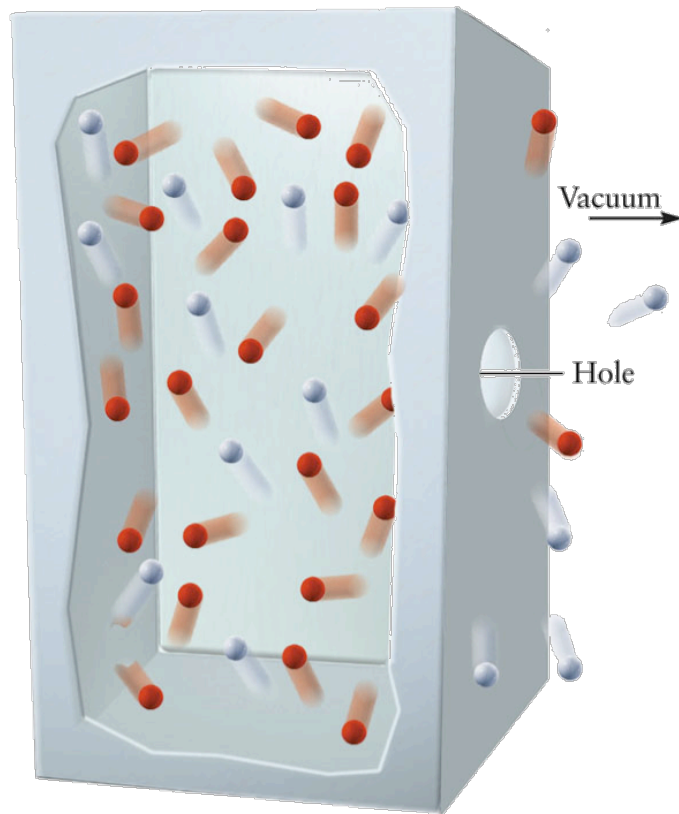
Diffusion and Effusion of Gases

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Diffusion – gradual dispersal of 1 substance through another

Effusion – escape of a gas through a small hole into a vacuum

Size of the hole is small vs the distance between particles



- Gas molecules collide w/ walls
- One side of wall has higher Pressure
- When a molecule “collides” with the hole, it escapes
- More chance of molecule colliding with hole on higher pressure side
- Overall – molecules escape through the hole

Graham's Law of Effusion

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Thomas Graham –

Constant T: rate inversely proportional to
square root of molar mass

$$Rate_{eff} \propto \sqrt{\frac{1}{M}}$$

Which suggests that:

When you compare effusion of different gases:

$$v_{ave} \propto \sqrt{\frac{1}{M}}$$

$$\frac{Rate_{eff}(A)}{Rate_{eff}(B)} = \sqrt{\frac{M_B}{M_A}}$$

$$\frac{Time_{eff}(A)}{Time_{eff}(B)} = \sqrt{\frac{M_A}{M_B}}$$



Temperature and Effusion

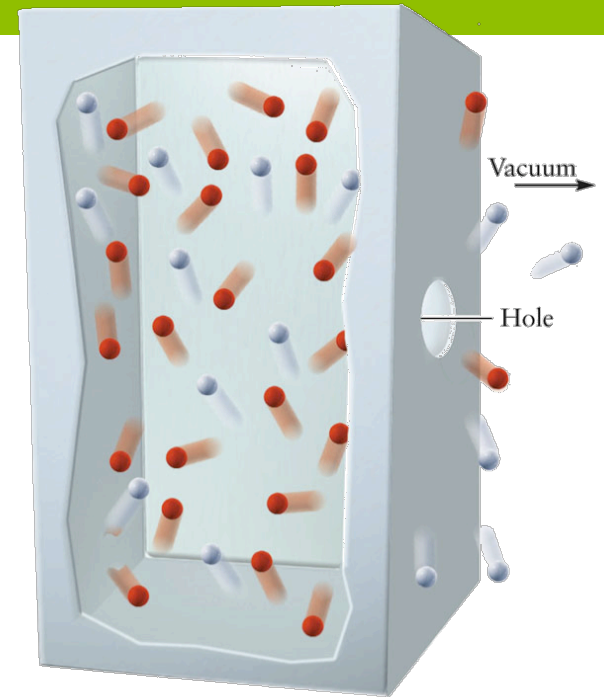
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Rate of effusion increases with the square root of the Temperature:

$$\frac{\text{Rate}_{eff}(T_1)}{\text{Rate}_{eff}(T_2)} = \sqrt{\frac{T_1}{T_2}}$$

Combined with:

$$v_{ave} \propto \text{Rate}_{eff}$$



$$v_{ave} \propto \sqrt{\frac{T}{M}}$$

The average speed of a gas is:

Proportional to

$$\sqrt{T}$$

Inversely proportional to

$$\sqrt{M}$$

Kinetic Theory of Gases

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Ideal Gas Law

Found experimentally through observation

$$PV = nRT$$

Summarizes the macroscopic properties of a gas

What about the microscopic behavior?

The behavior of individual gas atoms and molecules.

Kinetic Theory of Gases

Developed in 19th Century by:

Rudolf Clausius, James Clerk Maxwell and Ludwig Boltzmann

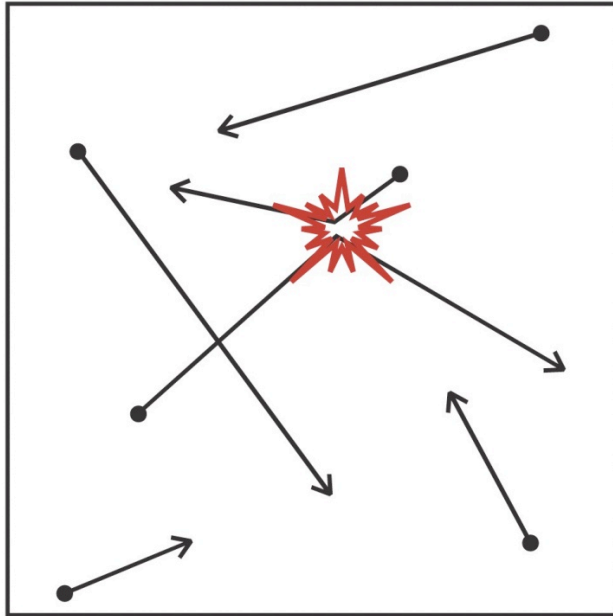
Uses a model of a gas and basic laws of physics to explain the measured properties of a gas

Microscopic understanding of Boyle's Law

Microscopic mechanical definition of Temperature

Kinetic Theory of Gases: Assumptions

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Kinetic Theory

Model based on gas particle motion

$KE = \text{Energy of translational motion}$

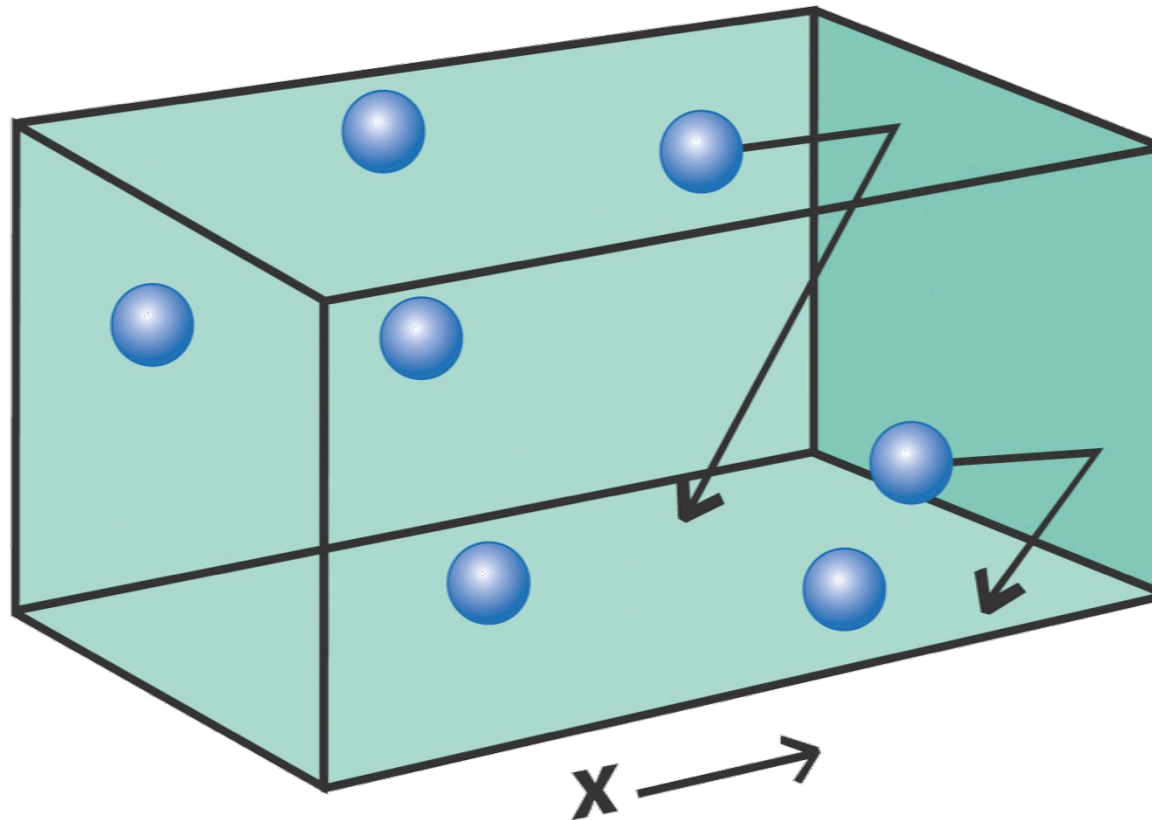
Assumptions about the gas molecules:

1. In continuous random motion
2. Infinitesimally small points
3. Move in straight lines until they collide
4. Do not influence each other except during a collision

Kinetic Theory:

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Pressure arises when gas molecules collide with a surface



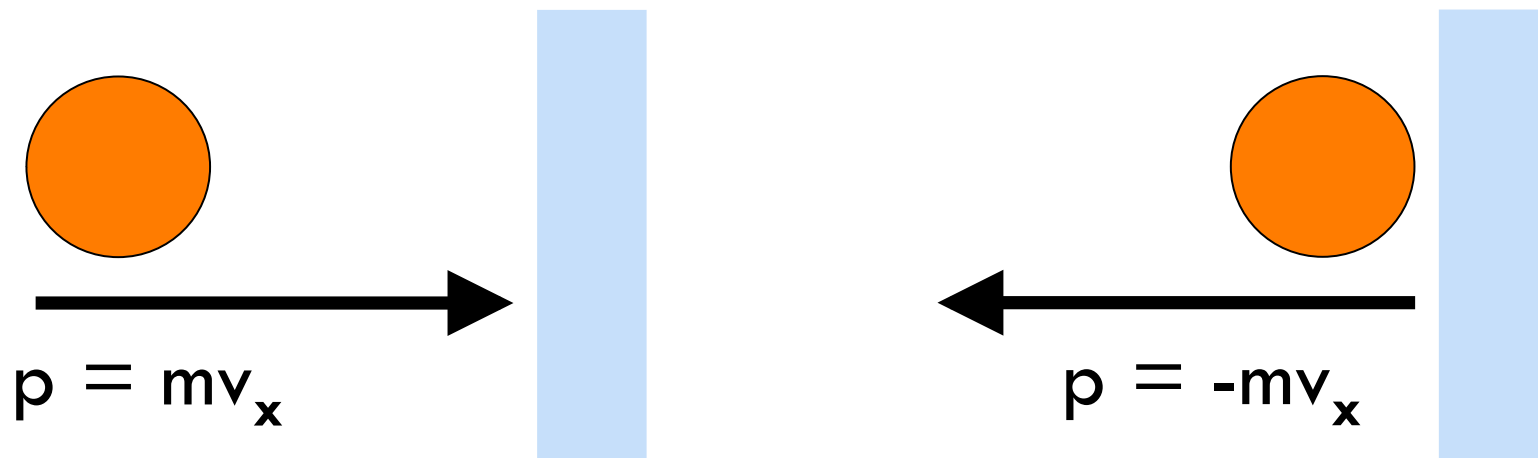
Can calculate the force of each impact and the rate of collisions

Kinetic Theory:

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1st step: Calculate change of momentum of one collision

Elastic collision with wall: $v_{\text{after}} = -v_{\text{before}}$

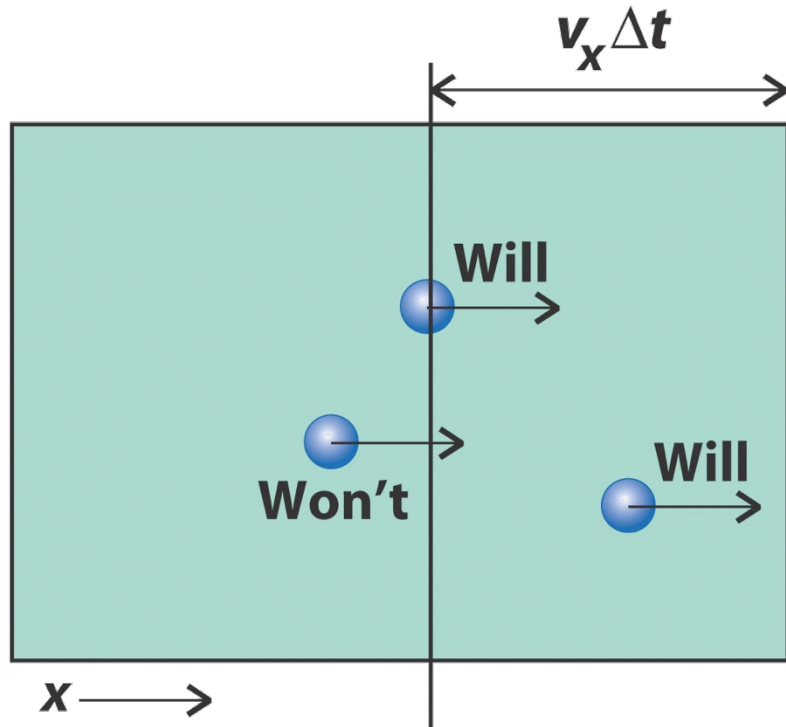


$$\Delta p_x = m(-v_x) - mv_x = -2mv_x$$

Next step: how many collisions in time Δt ?

Kinetic Theory:

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Collisions in time Δt :

In 1D:

All molecules within a distance

$$d = v_x \Delta t$$

In 3D:

All molecules within a volume

$$V = Av_x \Delta t$$

Number of molecules in $V = Av_x \Delta t$ is:

$$N_{Av_x \Delta t} = \frac{Av_x \Delta t}{V} \times N$$

Kinetic Theory:

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Half the molecules are moving towards the wall, so the Number of collisions is:

$$N_{coll} = \frac{1}{2} \frac{NAv_x \Delta t}{V}$$

Total Change in Momentum –

$$\Delta p_{tot} = \frac{1}{2} \frac{NAv_x \Delta t}{V} \times 2mv_x$$

$$\Delta p_{tot} = \frac{NmAv_x^2 \Delta t}{V}$$

Force = $\Delta p / \Delta t$

$$F = \frac{\Delta p_{tot}}{\Delta t} = \frac{NmAv_x^2}{V}$$

Kinetic Theory:

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

$$F = \frac{NmAv_x^2}{V}$$

$$\text{Pressure} = F/A$$

$$P = \frac{F}{A} = \frac{NmAv_x^2}{VA} \quad P = \frac{Nm v_x^2}{V}$$

Keep in mind, not all molecules have the same speed:

Use average speed

Now we relate $\langle v_x \rangle$ to the root-mean-square speed

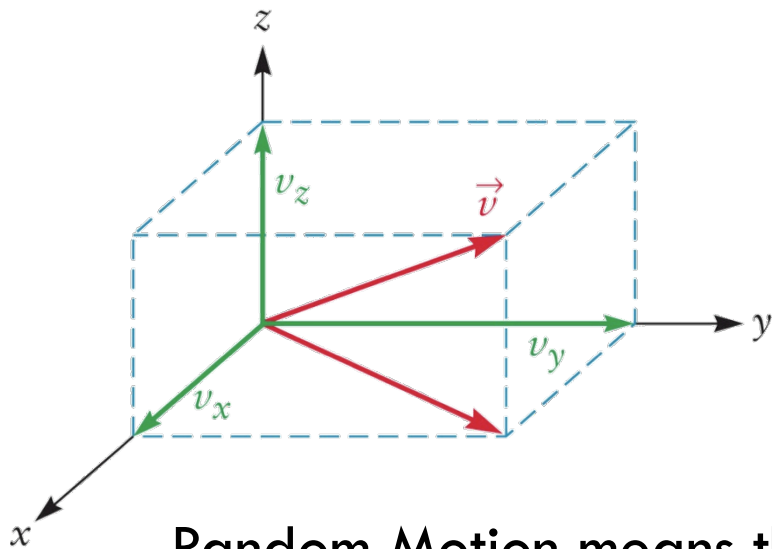
$$P = \frac{Nm \langle v_x^2 \rangle}{V}$$

$$v_{rms} = \sqrt{\langle v^2 \rangle}$$

Kinetic Theory:

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Speed vs. Velocity - Velocity is a vector which indicates direction of motion as well as rate of motion



$$v_{rms}^2 = \langle v^2 \rangle = 3 \langle v_x^2 \rangle$$

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

$$v_{rms}^2 = \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$$

$$\langle v_x^2 \rangle = \frac{1}{3} v_{rms}^2$$

Kinetic Theory:

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$$P = \frac{Nm \langle v_x^2 \rangle}{V} \quad \langle v_x^2 \rangle = \frac{1}{3} v_{rms}^2 \quad \longrightarrow \quad P = \frac{Nmv_{rms}^2}{3V}$$

$$N = nN_A \quad \longrightarrow \quad P = \frac{nN_A m v_{rms}^2}{3V}$$

$$M = mN_A \quad \longrightarrow \quad P = \frac{nM v_{rms}^2}{3V}$$

Boyle's Law as a function of
mean-square speed

$$PV = \frac{1}{3} nM v_{rms}^2$$

Kinetic Theory:

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Boyle's Law as a function of mean-square speed

$$PV = \frac{1}{3} nMv_{rms}^2$$

$$PV = nRT \quad \longrightarrow \quad nRT = \frac{1}{3} nMv_{rms}^2$$

$$3RT = Mv_{rms}^2 \quad \longrightarrow \quad v_{rms}^2 = \frac{3RT}{M}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

$$T = \frac{Mv_{rms}^2}{3R}$$

Kinetic Theory:

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What is the typical speed of a gas molecule?

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

Compare u_{rms} for

- a) He atom ($M = 4.0026 \text{ g/mol}$) at 298 K
- b) Xe atom ($M = 131.293 \text{ g/mol}$) at 298 K
- c) He atom ($M = 4.0026 \text{ g/mol}$) at 500 K

1360 m/s

238 m/s

1760 m/s

Maxwell-Boltzmann Distribution

51

Different molecules of gas have a distribution of speeds

James Clerk Maxwell: distribution of speeds based on molar mass (M) and temperature (T)

$$\Delta N = N f(v) \Delta v$$

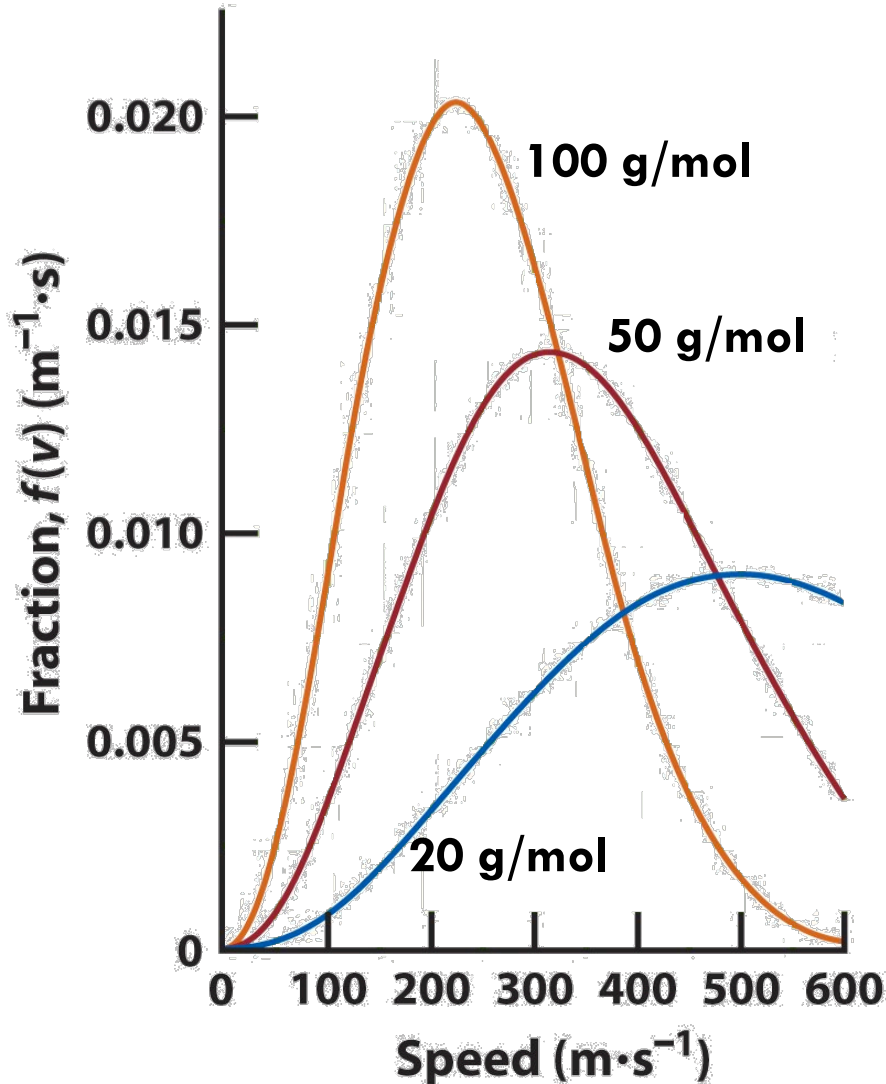
$\Delta N = \#$ gas molecules with speeds in the range

$v - (v + \Delta v)$

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

Maxwell-Boltzmann Distribution

52



$$\Delta N = N f(v) \Delta v$$

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

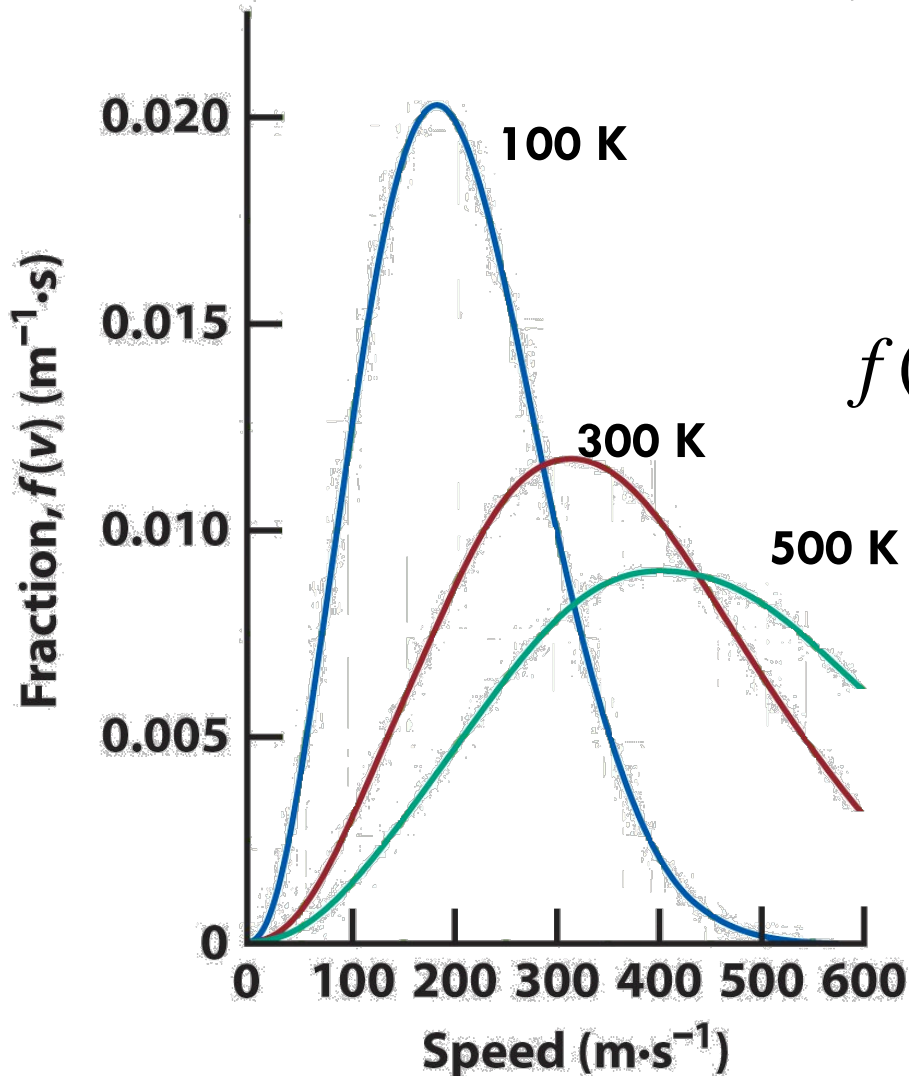
As M increases –

Average speed decreases

Range of speeds narrows

Maxwell-Boltzmann Distribution

53



$$\Delta N = N f(v) \Delta v$$

$$f(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 e^{-Mv^2/2RT}$$

As T increases –

Average speed increases

Range of speeds widens

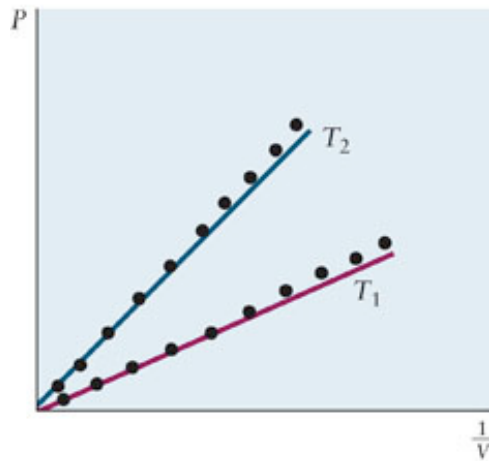
Real Gases

54

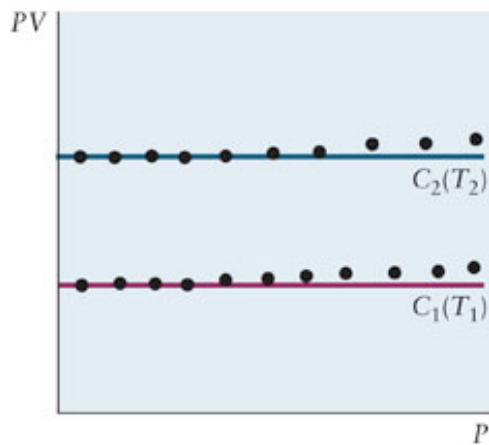
- Deviations from Ideal Behavior
- Van der Waals Equation
- Joule Thomson Effect

Real Gases

55



(b)



(c)

Ideal Gas Law: $PV = nRT$

What is an 'Ideal Gas'?

- Low P , High T
- Gas particles have $V = 0$
- No interactions between gas particles
- Collisions with walls are perfectly elastic
(KE of gas particles is conserved)

Real Gases

56

Both Quantitative and Qualitative observations show that the ideal gas model isn't perfect:

Quantitative Observations:

- When gases are cooled or compressed, they condense into liquid form
- Gas molecules must interact with each other – cohesion shows attractive forces
- Liquids are difficult to compress – repulsive forces between molecules!

Real Gases

57

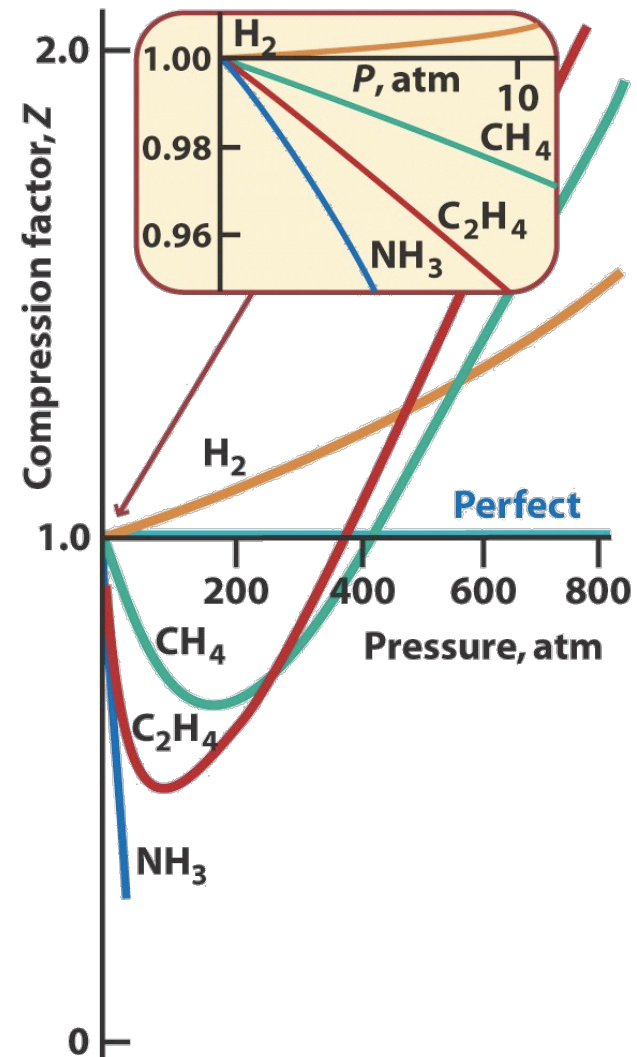
Qualitative Observations:

Compare the behavior of real gases to an ideal gas

Measure the compression factor Z :

$$Z = \frac{PV}{nRT}$$

For an Ideal Gas: $Z = 1$



Van der Waals Equation of State

58

$$PV = nRT$$

Ideal Gas Law Assumptions

- Gas particles have zero Volume
- Zero interactions between gas particles

What affect do attractive and repulsive forces between molecules have on the relationships between P,V,T?

Van der Waals Equation of State

59

Effect of repulsive forces:

Molecules cannot occupy the same space at the same time

Molecules exclude other molecules from the volumes they occupy

$$\text{Volume} \rightarrow V - nb$$

(b = excluded volume per mole)

Result of repulsive forces:

Molecules are pushed away from each other, toward walls

Increased collisions with walls



Increased P

Van der Waals Equation of State

60

$$P(V - nb) = nRT$$

Effect of attractive forces:

Molecules attracted to each other form pairs and clumps

Tendency to cluster reduces the effective # of gas 'molecules'

Rate of collisions with the wall is reduced, therefore P is reduced

$$P = \frac{nRT}{V - nb} - a \frac{n^2}{V^2}$$

Reduction in pressure:

Proportional to the square of N/V (pairs of molecules)

a depends on the strength of the attractive forces

Van der Waals Equation of State

61

$$P = \frac{nRT}{V - nb} - a \frac{n^2}{V^2} \longleftrightarrow \left(P + a \frac{n^2}{V^2} \right) (V - nb) = nRT$$

TABLE 9.3 van der Waals Constants of Several Gases

Name	Formula	a (atm L ² mol ⁻²)	b (L mol ⁻¹)
Ammonia	NH ₃	4.170	0.03707
Argon	Ar	1.345	0.03219
Carbon dioxide	CO ₂	3.592	0.04267
Hydrogen	H ₂	0.2444	0.02661
Hydrogen chloride	HCl	3.667	0.04081
Methane	CH ₄	2.253	0.04278
Nitrogen	N ₂	1.390	0.03913
Nitrogen dioxide	NO ₂	5.284	0.04424
Oxygen	O ₂	1.360	0.03183
Sulfur dioxide	SO ₂	6.714	0.05636
Water	H ₂ O	5.464	0.03049

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$$Z = \frac{PV}{nRT} = \frac{V}{V - nb} - \frac{a n}{RT V}$$

$Z > 1$ Repulsive forces dominate

$Z < 1$ Attractive forces dominate

Real vs Ideal Gas

62

A sample of 8.00 kg of gaseous nitrogen fills a 100.-L flask at 300. °C.

Calculate the pressure of the gas as real gas, and as an ideal gas.

Do attractive or repulsive forces dominate?

$$P = \frac{nRT}{V - nb} - a \frac{n^2}{V^2}$$

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Joule Thomson Effect

63

Gases can be liquified by reducing T

Lower T corresponds to lower v_{rms}

.... Slower molecules means lower temperature

Remember, we now consider interactions between molecules

As particles separate, they are moving against pull of PE

Particles moving “uphill” will slow down

Joule – Thomson Effect - Real gases cool as they expand

