

CHEM 1300

Week 5 - 8

Lectures 5 to 8 (Week 5 to 8):

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Chapter 10: Gases

Chapter 14: Chemical Kinetics

Chapter 15: Chemical Equilibrium

Chapter 5: Thermochemistry

1

Gases

(Chapter 10)

1. Pressure
2. Gas Laws
3. Ideal gas equation
4. Kinetic-molecular theory of gases
5. Molecular diffusion



2

Characteristics of Gases

- The atmosphere is composed of gaseous mixture of oxygen and nitrogen – air.
- Unlike liquids and solids, gases
 - **expand to fill** in the containers.
 - are highly **compressible**.
 - have relatively **low** densities.
- Two (or more) gases mix together to form a homogenous mixture.

3

Pressure

- Gases exert a pressure on any contacting surface.
- Pressure is defined as the amount of **force** applied to the **area** of surface.

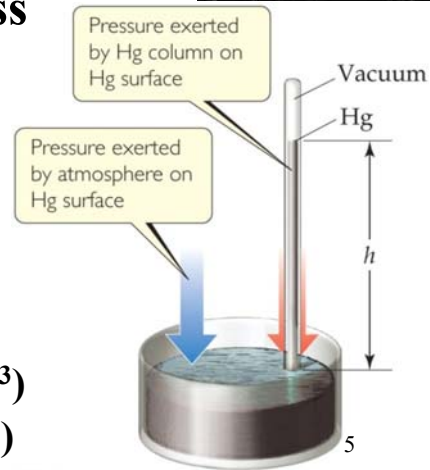
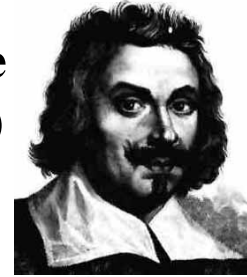
$$[\text{N m}^{-2}] \quad \boxed{P = \frac{F}{A}} \quad \begin{matrix} [\text{N}] \\ [\text{m}^2] \end{matrix}$$

- Units of pressure
 - Pascal : $1 \text{ Pa} = 1 \text{ N m}^{-2}$
 - Bar: $1 \text{ bar} = 10^5 \text{ Pa} = 100 \text{ kPa}$

4

Measurements of pressure

- **Barometer** was invented to measure the atmospheric pressure by the heights (h) of mercury columns by **Torricelli**.
- In atmosphere, an inverted glass tube, completely filled with mercury (Hg), exerts a column height of **76 cm** on a dish of mercury.



$$P = h \rho g$$

ρ – density of mercury ($13.59 \times 10^3 \text{ kg m}^{-3}$)

g – acceleration due to gravity (9.81 m s^{-2})

- The mass of mercury column is balanced by the external pressure:

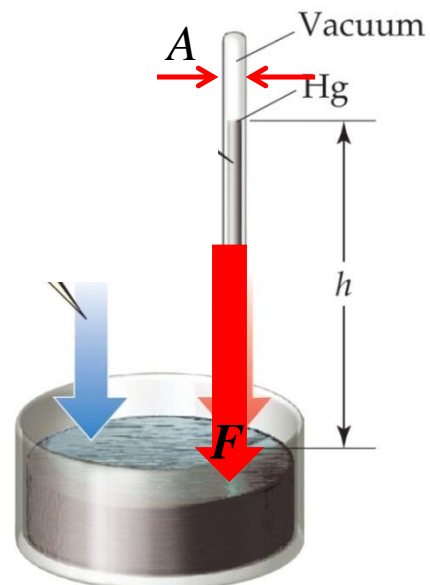
$$F = m g$$

$$F = V \rho g$$

$$F = h A \rho g$$

$$P = \frac{F}{A} = \frac{h \cancel{A} \rho g}{\cancel{A}}$$

$$P = h \rho g$$



m – mass of mercury column

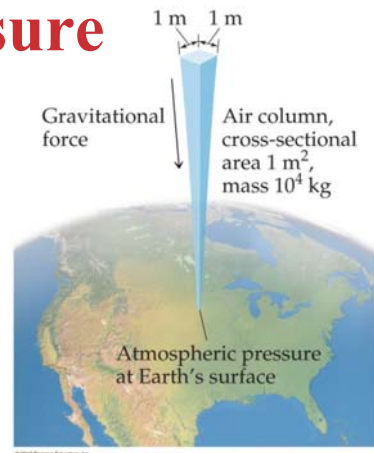
A – cross sectional area of column

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Atmospheric pressure

- One atmospheric pressure (**atm**) is equal to:

- 760 mm Hg
- 760 Torr
- 101325 Pa or N m^{-2}
- 1.01325 bar



- An air column (cross-sectional area $\approx 1 \text{ m}^2$) of mass 10,000 kg, extends through the entire atmosphere on earth.
- Blood pressure is expressed in the unit of **mmHg** or **Torr**.



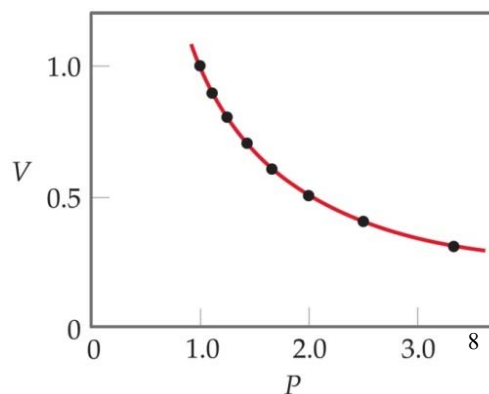
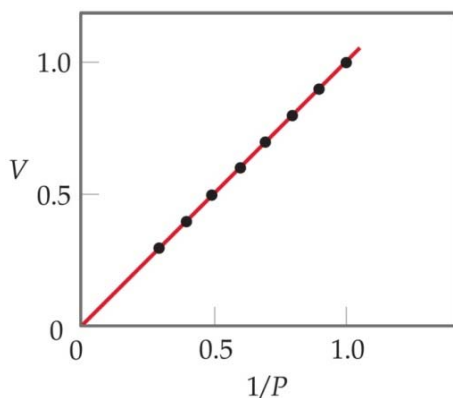
7

The pressure – volume relationship: Boyle's Law

- The volume of a fixed quantity of gas at constant temperature is inversely proportional to the pressure.



$$V = \text{constant} \times \frac{1}{P} \quad \text{or} \quad PV = \text{constant}$$



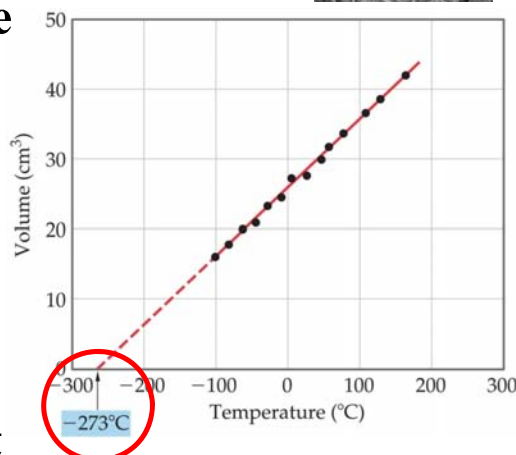
The temperature – volume relationship: Charles's Law



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

$$V \propto T$$

- A plot of V versus T is a straight line.
- Extrapolation of $V - T$ plot gives to the T of $-273\text{ }^{\circ}\text{C}$.



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

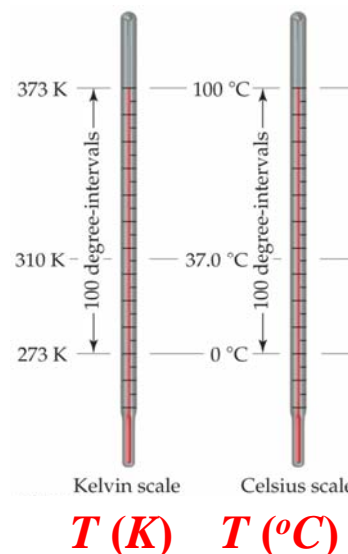
Temperature scale



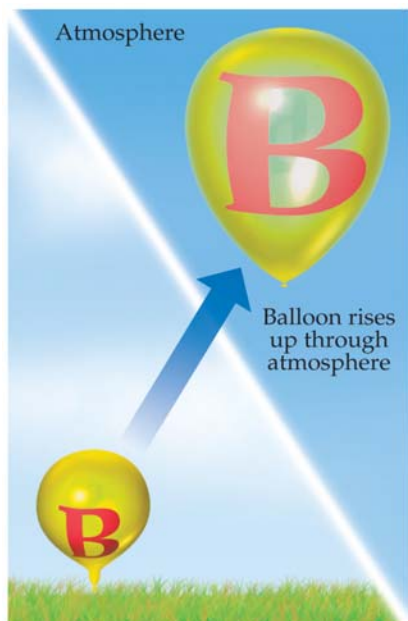
- The absolute temperature scale was proposed by William Thomson, 1st Baron Kelvin in 1848.

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

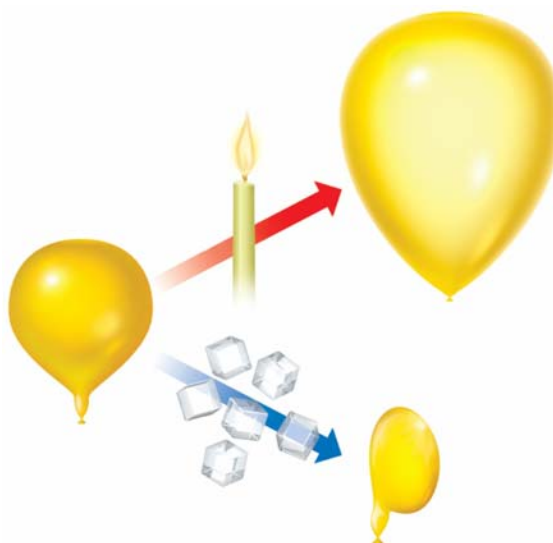
- On this scale, 0 K called *absolute zero*, equals $-273.15\text{ }^{\circ}\text{C}$.



Boyle's Law and Charles's Law



Does atmospheric pressure increase or decrease as altitude goes high?



Balloon changes its volume when it is heated up or cooled down.

11

The quantity – volume relationship: Avogadro's Law

- The volume of a gas at constant temperature and pressure is directly proportional to the **number of moles** (n) of the gas.

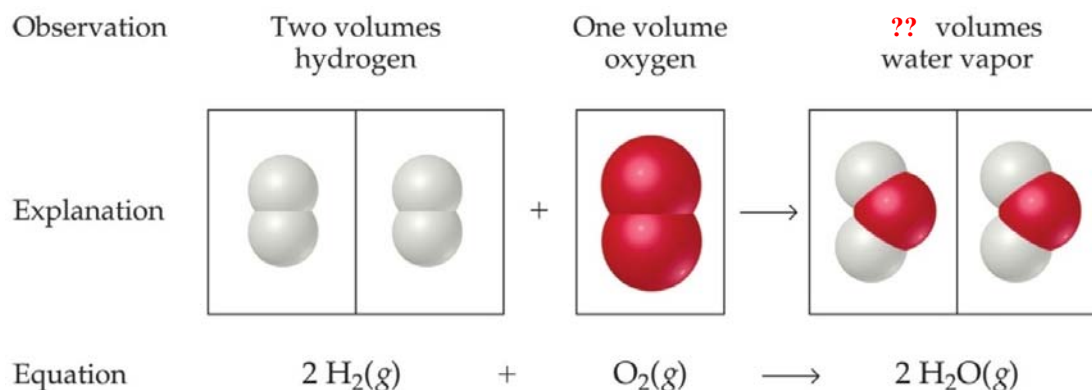


- Mathematically, this means $V = \text{constant} \times n$

Avogadro's hypothesis

Equal volume of gases at the same T and P contain equal numbers of molecules.

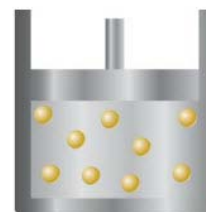
	He	N ₂	CH ₄
Volume	22.4 L	22.4 L	22.4 L
Pressure	1 atm	1 atm	1 atm
Temperature	0 °C	0 °C	0 °C
Mass of gas	4.00 g	28.0 g	16.0 g
Number of gas molecules	6.02×10^{23}	6.02×10^{23}	6.02×10^{23}



Describe what happens to the volume of gases after the reaction.

13

Describe what happens to gas cylinder (with a movable piston) subjected to following changes:



Changes	Comments
(A) Heating the gas at constant pressure	
(B) Reducing the volume at constant temperature	
(C) Injecting additional gas, keeping temperature and volume constant	

14

Ideal-Gas Equation

Boyle's law: $V \propto \frac{1}{P}$

Charles's law: $V \propto T$

Avogadro's law: $V \propto n$

- Combining all three equations, we get

$$V \propto \frac{nT}{P} \quad \text{or} \quad V = \underbrace{\text{constant}}_R \times \frac{nT}{P}$$

15

Universal gas constant

- The constant of proportionality is known as R , the gas constant.

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

$$PV = nRT$$

Units	Numerical Value
L-atm/mol-K	0.08206
J/mol-K*	8.314
cal/mol-K	1.987
m ³ -Pa/mol-K*	8.314
L-torr/mol-K	62.36

*SI unit.

- The value of R is determined by the measurement that 1 mole of an ideal gas occupies a volume of 22.414 liter at 1 atm and 0 °C (273.15 K).
- The condition of 1 atm and 0 °C is referred as **standard temperature and pressure (STP)**.

16

Ideal gas law in term of gas density

$$PV = nRT$$

$$PV = \frac{m}{M} RT$$

← mass

$$\frac{m}{V} = \frac{PM}{RT}$$

← molar mass



CO₂ (as fire extinguisher agent) is denser than air.



Hot-air balloon

Helium balloon



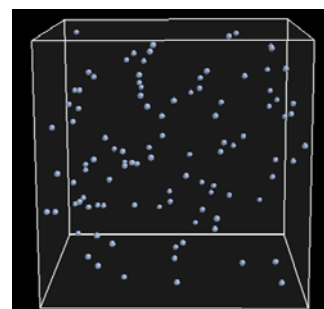
Mass density of the gas:

$$d = \frac{m}{V} = \frac{PM}{RT}$$

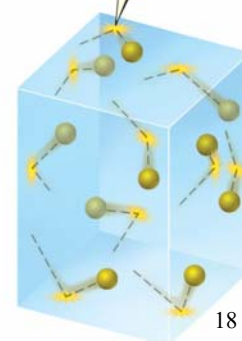
Kinetic-Molecular theory of gases

It states that:

1. Gases consist of large numbers of molecules that are in **continuous** and **random** motion.
2. The occupied volume of all gaseous molecules is negligible.
3. **Attractive** and **repulsive** forces between gas molecules are negligible.



Pressure inside container comes from collisions of gas molecules with container walls



Kinetic-Molecular theory of gases

4. Energy is transferred between molecules during collisions.

The **average** kinetic energy (K.E.) of the molecules is proportional to the absolute temperature of gas.

$$\text{Average K.E.} = \frac{3}{2} kT$$

where k is Boltzmann constant.
($1.381 \times 10^{-23} \text{ J K}^{-1}$)

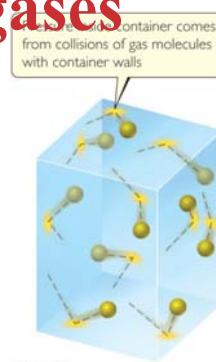
At a given temperature, all gas molecules in a mixture have the same **average** kinetic energy, independent of molecular masses.

19

Kinetic-Molecular theory of gases

The theory explains both pressure and temperature at molecular level:

- The pressure of a gas is caused by **collisions** of atoms/molecules with the container walls.
 - A **smaller** box experiences **more** collisions by gases.
 - $V \downarrow \Rightarrow P \uparrow$
- The absolute temperature of a gas is a measure of **average** kinetic energy.
 - A **higher** temperature allows molecules to move **faster** and make **more** collisions.
 - $T \uparrow$ at constant $V \Rightarrow P \uparrow$.



20

Distribution of molecular speed

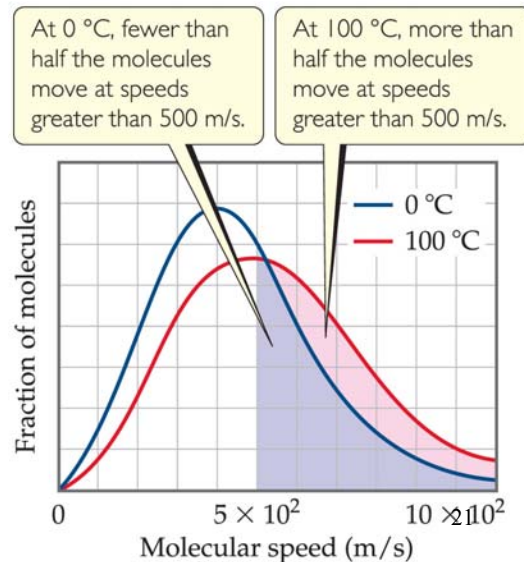
- Molecules make collisions, the individual molecules move at **different** speeds – **speed distribution**.

$$\text{Average K.E.} = \frac{1}{2} m u^2$$

$$\Rightarrow u = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

m is mass of molecule.

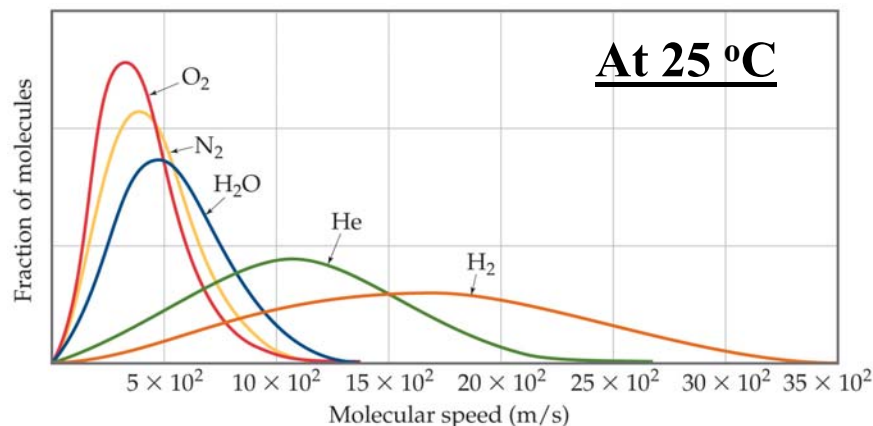
u is the **root-mean-square** (*rms*) speed.



RMS speed

- Different gases have different *rms* speeds at a given temperature.
- The **lighter** the molecule, the **faster** it moves, the **higher** its *rms* speed.

$$u = \sqrt{\frac{3RT}{M}}$$



Molecular diffusion

- Molecules are in constant and random motion and tend to move from regions where they are in higher concentration to regions where they are less concentrated – **Diffusion**.
- Smell of perfume – the perfume molecules in the bottle diffuse and mix with the molecules of air in the room.

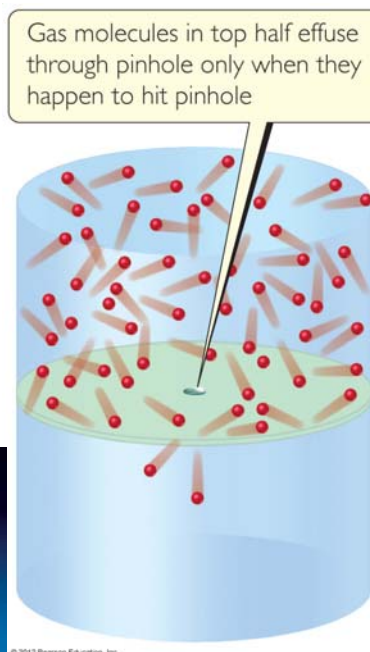


E.g. Diffusion of Bromine
http://www.youtube.com/watch?v=_oLPBnhOCjM

23

Molecular effusion

- The escape of molecule through a tiny hole – **effusion**.
- Smell of food comes out from a sealed plastic bag or wrapper through some invisible tiny holes.



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24

Graham's law

- Diffusion / effusion rate (r) depends on the speed of molecules :

$$r \propto u = \sqrt{\frac{3kT}{m}}$$

- At same T , the **ratio** of diffusion rate between two gases of different masses is:

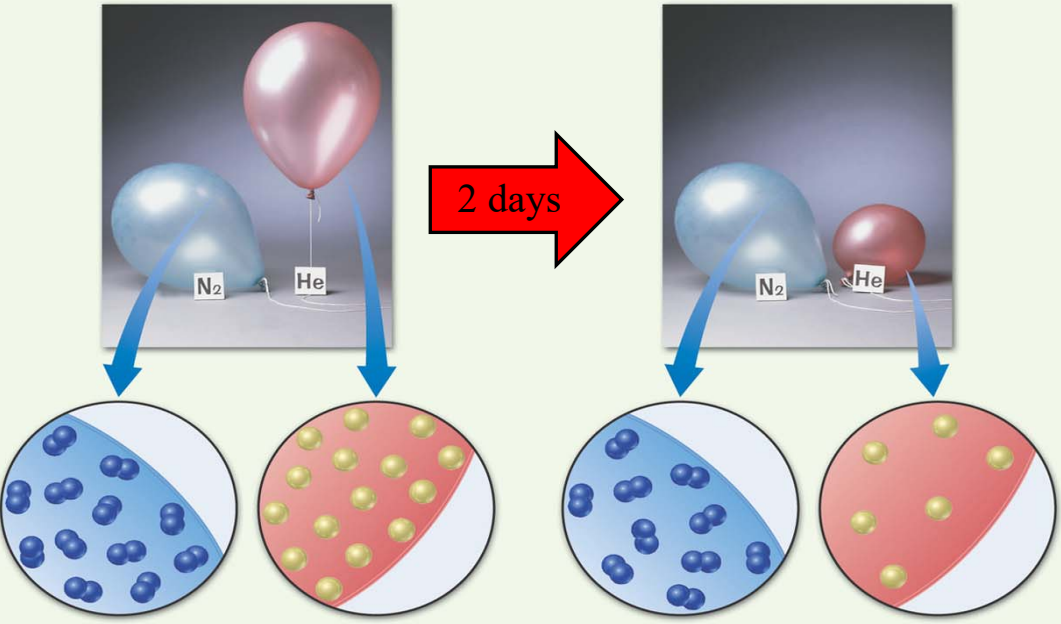
$$\frac{r_1}{r_2} = \sqrt{\frac{m_2}{m_1}}$$

where m_1 and m_2 is the masses of gases 1 and 2.

- Gas of lighter mass **diffuse faster** than gas of heavier mass.

25

GRAHAM'S LAW OF EFFUSION
The effusion rate of a gas is inversely proportional to the square root of its molar mass. Gas effuses through pores of a balloon. At identical pressure and temperature, the lighter gas effuses more rapidly.



Two balloons are filled to the same volume, one with helium and one with nitrogen.

After 48 hours, the helium-filled balloon is smaller than the nitrogen-filled one because helium escapes faster than nitrogen.

26