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BSK1133 PHYSICAL CHEMISTRY

CHAPTER 1
KINETIC THEORY OF GASES
(PART A)

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Description

Aims

- To understand the properties of gases.
- To study the kinetic theory of gases.

Description

Expected Outcomes

- ❖ Able to understand the properties and importance law of gases
- ❖ Able to understand the kinetic theory of gases at different properties changes

References

- ✓ Atkins, P & Julio, D. P. (2006).Physical Chemistry (8th ed.). New York: Oxford.
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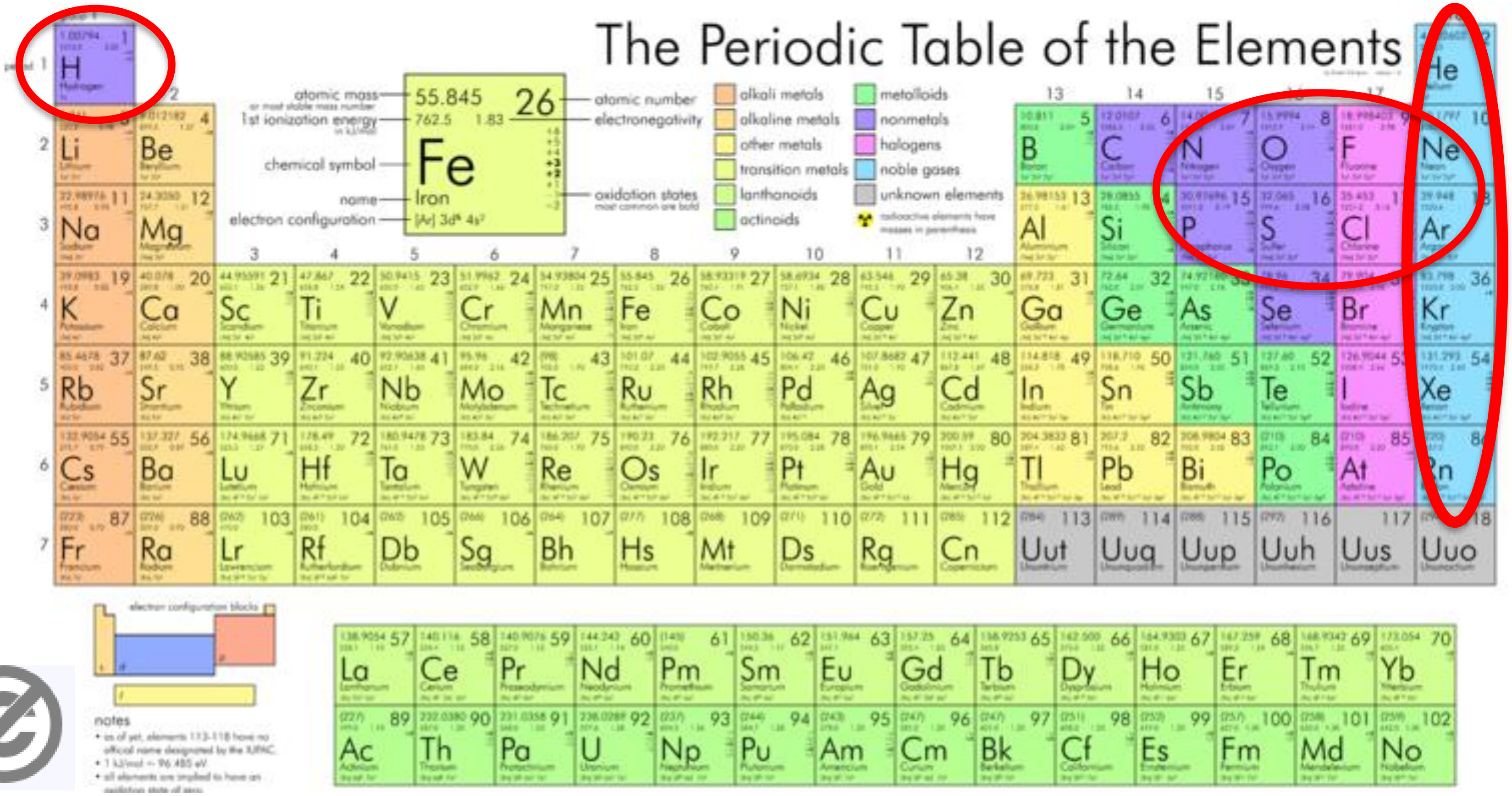
- ✓ Silbey, R. J., Alberty, A. A., & Bawendi, M. G. (2005). Physical Chemistry. New York: John Wiley & Sons.
- ✓ Mortimer R. G. (2008) Physical Chemistry, Third Edition , Elsevier Academic press, USA.

Contents

1.1 Gases and its properties

Gases

Elements that exist as gases at room temperature (25^0C) and 1 atmosphere



Sources:
2012rc
https://commons.wikimedia.org/wiki/File:Periodic_table_large.png

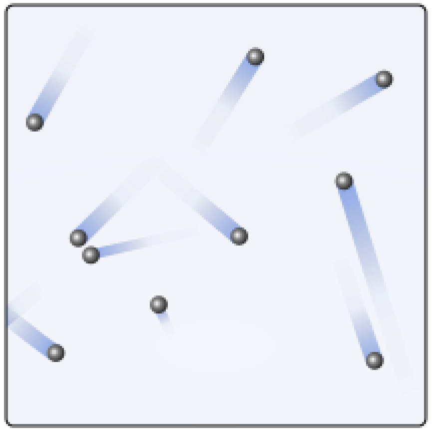
Compressibility of Gases

- Unlike a liquid or solid which has its atomic particles in contact with one another, gas particles are **far apart**, colliding with one another and bouncing off in different directions. This means that a gas has **no definite shape or volume** and will expand to fill the container.
- Since gas has a great distance between its particles, gas has lower density as compared to solid or liquid; can be compressed.

Properties of Gases

Property	Description	Unit(s) of Measurement
Pressure (P)	The force exerted by gas against the walls of the container	atm, mmHg, torr, kPa
Volume (V)	The space occupied by the gas	L, mL
Temperature (T)	Determines the kinetic energy and rate of motion of the gas particles	°C, K
Amount of gas (n)	The quantity of gas present in a container	g, mol

Gas Pressure



Gas particles are extremely small. Thus, billions of the gas particles will hit the walls of a container and exerts a force which known as pressure (Pressure = Force / Area).

The gas pressure is increased by increasing the frequency of collisions between gas particles and the walls of the container.

The frequency of collisions can be increased by:

1) **Increasing the temperature of the gas:**
At higher temperatures, the movement of gas particles is faster and hitting the walls of container with more force and higher frequency. As a result, the gas pressure increases.

2) **Increasing the number of moles (n) (increasing the concentration of gas particles):**
Increasing the concentration of gas particles inside a container has resulted in increasing the collision frequency between the gas particles and the walls of the container; leading to an increase in the gas pressure inside the container. The unequal concentration of gas particles on either sides of the walls of the container causes a pressure differential to develop across the walls of the container.

Atmospheric Pressure:

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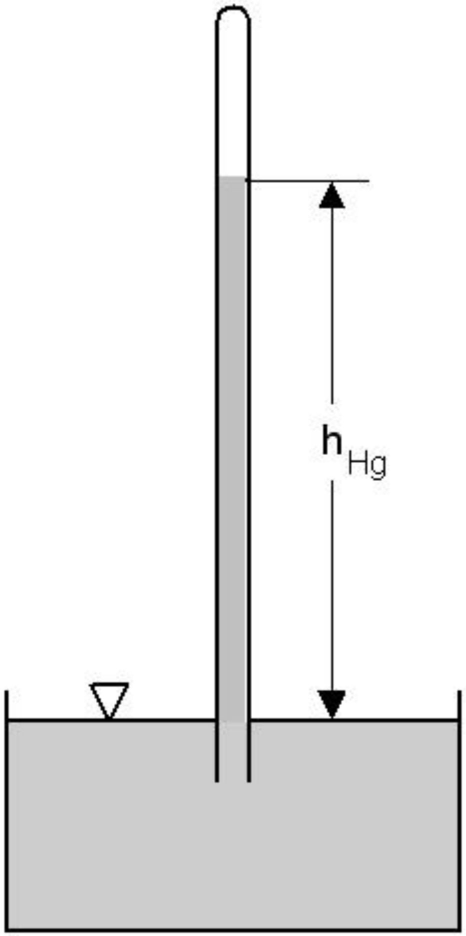


Sources:
Volker Sperlich
https://commons.wikimedia.org/wiki/File:Prinzip_Torricelli.jpg

- ✓ At the ground surface of the Earth, gravitation causes the column of air above it to exert a pressure equals to 1 atmosphere (atm). This pressure is defined as the **atmospheric pressure**.
- ✓ **Mercury barometer** can be use to measure the atmospheric pressure. The pressure of 1 atmosphere at sea level causes the mercury column in the barometer to rise to **760 mmHg** (millimeters of mercury) high:

1 atm = 760 mmHg = 760 torr

- ✓ The **mmHg** is also known as the **torr**, named in honor of the Evangelista Torricelli who invented the barometer.

Unit Measuring Pressure:

Unit	Abbreviation	Unit equivalent to 1 atm
Atmosphere	atm	1 atm (exact)
Molimeters of Hg	mmHg	760 mmHg
Torr	torr	760 torr
Pounds per square inch	Lb/in2 (psi)	14.7 psi
Kilopascal	kPa	101.325 kPa

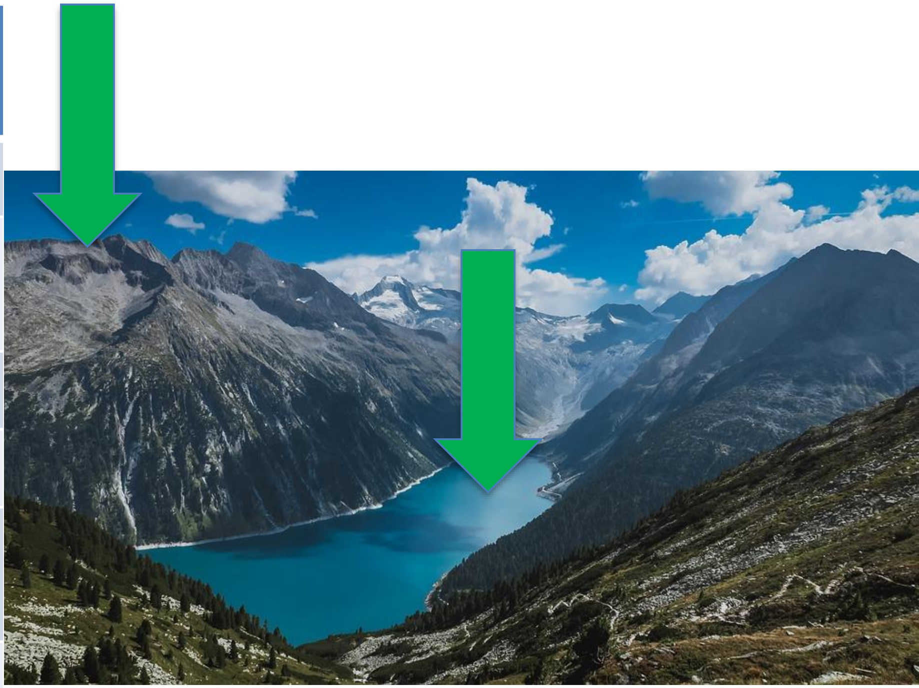
Unit SI : Pascal (Pa)

1 bar = 100,000 Pa

Effect of atmospheric pressure to altitude:

Atmospheric pressure changes with altitude. As one ascends altitude, the air becomes less dense, causing lower atmospheric pressure. Conversely, in Death Valley, which is 282 feet below sea level, the air is denser and atmospheric pressure is greater.

Location	Altitude (km)	Atmospheric Pressure (mmHg)
Sea level	0	760
Los Angeles	0.009	752
Las Vegas	0.70	700
Denver	1.60	630
Mount Whitney	4.50	440
Mount Everest	8.90	253



Sources: https://pixabay.com/en/landscape-mountain-mountain-peak-1869192/

Effect of atmospheric pressure to weather:

Variations in weather also cause changes in atmospheric pressure. On a hot sunny day, the pressure on the mercury surface increases, causing the mercury column to rise to indicate a higher atmospheric pressure (weather report: high pressure system). Conversely, low pressure was found on a rainy day and the mercury column drops (weather report: low pressure system).

1.2 Gas laws

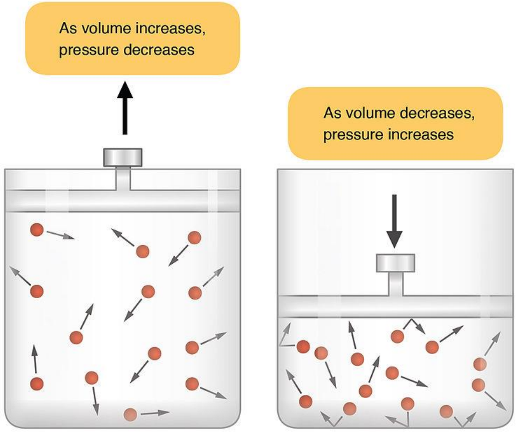
Boyle's Law : Pressure vs Volume

In a piston-cylinder system, a movable, frictionless piston encloses an amount of n moles of a gas. When the **volume** of the gas decreases by one-half by compressing the cylinder, the **pressure** of the gas increases two-fold. This **inverse relationship** between volume and gas pressure is known as **Boyle's law**:

$$P_1 V_1 = P_2 V_2$$

Product PV = Constant

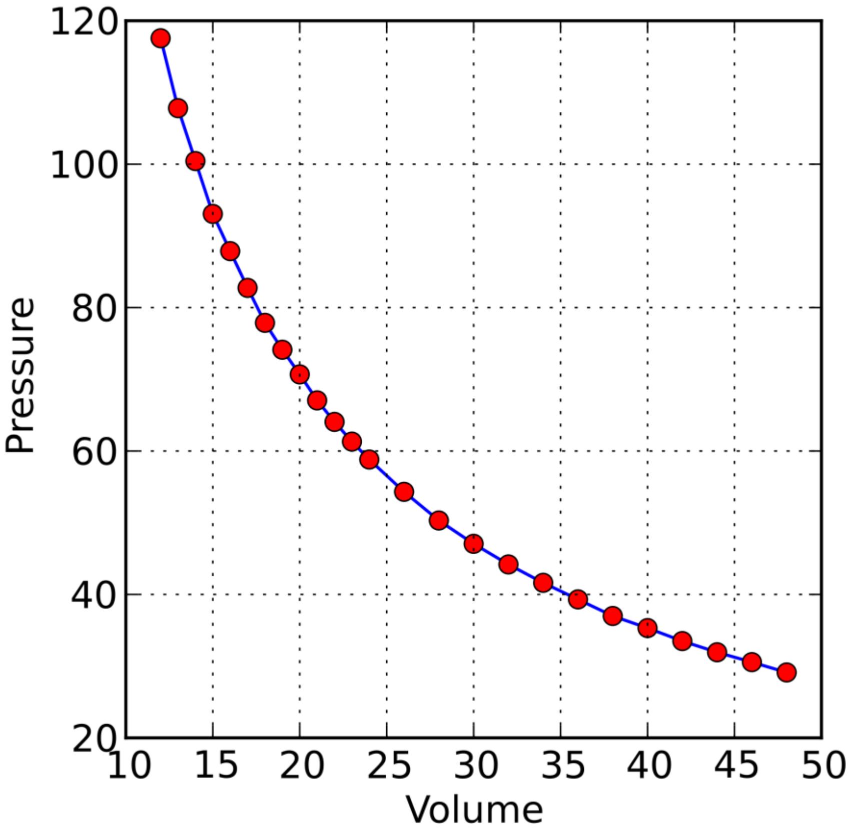
P and V show an inverse relationship.



Sources:
OpenStax College
https://commons.wikimedia.org/wiki/File:2314_Boyles_Law.jpg

Conditions for Boyle's Law:

1) **n moles** of gas particles remain **constant**.
2) **temperature** in chamber remains **constant**.



Sources:
Krishnavedala
https://commons.wikimedia.org/wiki/File:Boyles_Law.svg

$P \propto 1/V$

$P \text{ X } V = \text{CONSTANT}$

$P_1 \text{ X } V_1 = P_2 \text{ X } V_2$

Constant temperature
Constant amount of gas

Charles' Law : Temperature vs Volume

In 1787, **Jacques Charles**, a French physicist and a balloonist has proposed Charles' law which stated that:

The volume of a gas is directly proportional to the temperature (in Kelvin) at constant pressure and amount of gas (in moles).

Charles' law can be written as:

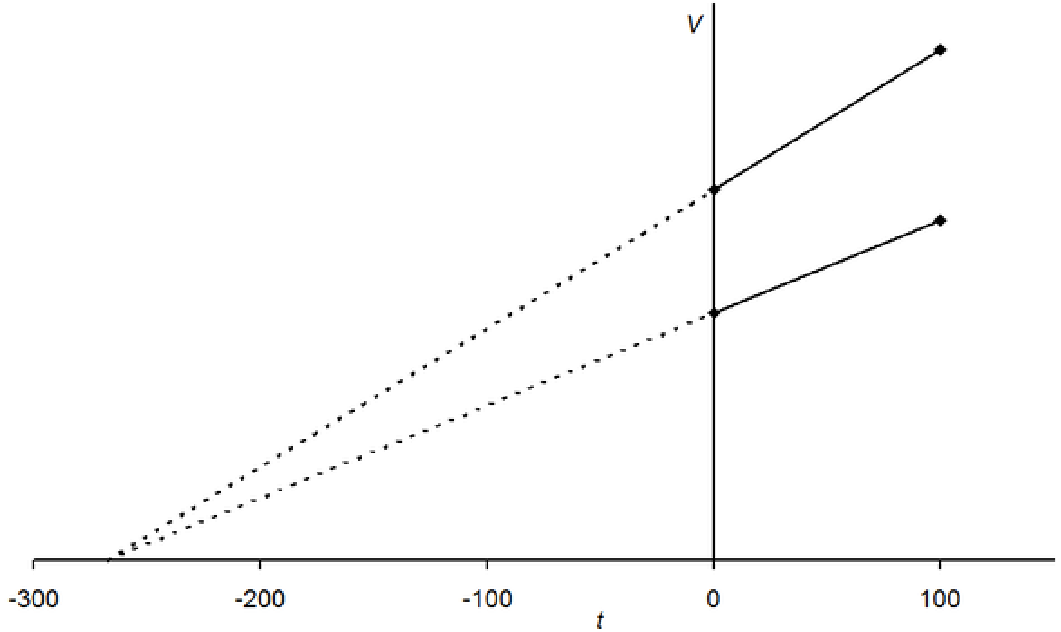
$$V \propto T \text{ or } V_1 / T_1 = V_2 / T_2$$

Temperature and Volume show a direct relationship.

Conditions for **Charles' Law**:

1) **n moles** of gas particles remain **constant**.

2) **pressure** in chamber remains **constant**.



Sources:
Physchim62
https://commons.wikimedia.org/wiki/File:Charles%27s_law_graph.png

$V \propto T$

$V = \text{constant x } T$

$V_1/T_1 = V_2/T_2$

Temperatures must be expressed in unit **Kelvin**.

Gay Lussac's Law : Temperature vs Pressure

Gay-Lussac propounded a gas law that relates the **temperature** to the **pressure** of the gas; known as **Gas-Lussac's Law:**

The pressure of a gas is directly proportional to its temperature (in Kelvin).

Increasing temperature will increase the pressure of the gas, at constant volume and number of moles (n).

$$P_1 / T_1 = P_2 / T_2$$

Conditions for Gay Lussac's Law:

1) **n moles** of gas particles remain **constant**.

2) **volume** of system remains **constant**.

Combined Gas Law

The **Combined Gas Law is the** relationships among the conditions of pressure, volume and temperature for gases which the *amount of gas (in moles) is remained constant*.

Combined gas law:

$$P_1 V_1 / T_1 = P_2 V_2 / T_2$$

Avogadro's Hypothesis

Avogadro's hypothesis stated that:

Equal number of molecules consists of the same volumes of gases at constant temperature and pressure.

$$V_{1} / n_{1} = V_{2} / n_{2}$$

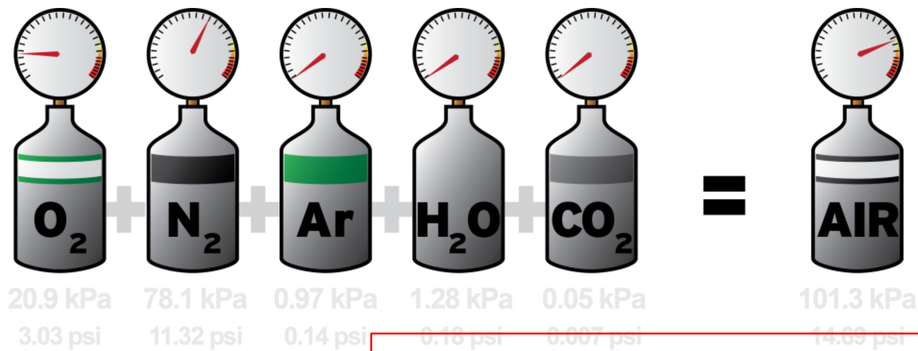
Conditions for Avogrado's Law:

1) **Temperature** of gas particles remain **constant**.
2) **Pressure** of system remains **constant**.

Example:

22.414 L of any gas consists of 6.022 X 10^{23} atoms (or molecules) at 1 atm and 0 °C.

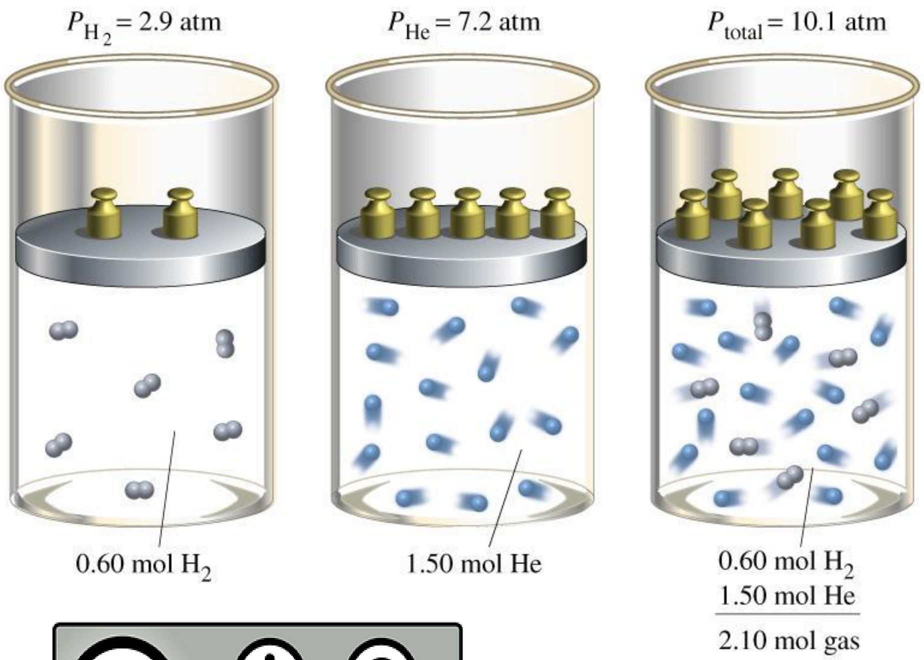
Dalton's Law



Sources:
https://ar.wikipedia.org/wiki/%D9%85%D9%84%D9%81:Dalton%27s_law_of_partial_pressures.png

Dalton's Law of Partial Pressure states that the total pressure (P_{total}) for a mixture of unreactive gases is the sum of the partial pressures (P_n) of individual gases.

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



Sources:
Dr. Blair Jesse Ellyn Reich
https://commons.wikimedia.org/wiki/File:Presiones_parciales.JPG

V and *T* are **constant**

As shown in the figure:

Tank A: hydrogen gas (H_2) at 2.9 atm.

Tank B: helium gas (He) at 7.2 atm.

Tank C: total pressure of H_2 + He is 10.1 atm.

Condition:

3 tanks are same the volume and temperature.

Number of gas molecules determines the gas pressure in a container regardless the type of gas.

Example: Gas A and gas B are in a container of volume V

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

n_A is the number of moles of A

$$P_B = \frac{n_B RT}{V}$$

n_B is the number of moles of B

$$P_T = P_A + P_B \qquad X_A = \frac{n_A}{n_A + n_B} \qquad X_B = \frac{n_B}{n_A + n_B}$$

$$P_A = X_A P_T \qquad P_B = X_B P_T$$

$$P_i = X_i P_T$$

mole fraction $(X_i) = \frac{n_i}{n_T}$

Using Mole Fraction to Calculate Partial Pressure of A Gas:

The partial pressures of the component gases in a mixture can be calculated by knowing the amounts (in moles) and the total gas pressure (P_T) of the gas mixture.

Example: A gas mixture contains 3 different gases: A, B, and C. There are n_A moles of A, n_B moles of B, and n_C moles of C.

The total number of moles (n_T) of gases in a mixture, $n_T = n_A + n_B + n_C$

Hence, the mole of the individual gas can be expressed as the **mole fraction X**:

$$X_A = \frac{n_A}{n_A + n_B + n_C} = \frac{n_A}{n_T}$$

The partial pressure of gas component A, P_A, can be determined by multiplying its mole fraction with the total gas pressure P_T:

$$P_A = X_A P_T$$

Ideal Gas Equation

Boyle's law: $V \propto \frac{1}{P}$ (at constant *n* and *T*)

Charles' law: $V \propto T$ (at constant *n* and *P*)

Avogadro's law: $V \propto n$ (at constant *P* and *T*)

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

$$V = \text{constant} \times \frac{nT}{P} = R \frac{nT}{P}$$

R is the **gas constant**

Boyle's Law :

Increasing or decreasing the volume of a gas at a constant temperature. $P = (nRT)\frac{1}{V};\quad nRT \text{ is constant}$

Charles' law:

Heating or cooling a gas at constant pressure.

$$V = \frac{nR}{P}T;\quad \frac{nR}{P} \text{ is constant}$$

Heating or cooling a gas at constant volume.

$$P = \frac{nR}{V}T;\quad \frac{nR}{V} \text{ is constant}$$

Avogrado' law:

Dependence of volume on amount of gas at constant temperature and pressure.

$$V = \frac{RT}{P}n;\quad \frac{RT}{P} \text{ is constant}$$

Ideal Gas Equation: $PV = nRT$

The conditions 0 ^{0}C and 1 atm are called **standard temperature and pressure (STP).**

$$PV = nRT$$

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

$$R = 0.082057\text{ L} \cdot \text{atm} / (\text{mol} \cdot \text{K})$$

1.3 Calculations

Density and Molar Mass Calculation

Density (ρ) Calculations

$$\rho = \frac{m}{V} = \frac{P\mathcal{M}}{RT}$$

m is the mass of the gas in g

$\mathcal{M}$ is the molar mass of the gas

Molar Mass ($\mathcal{M}$) of a Gaseous Substance

$$\mathcal{M} = \frac{\rho RT}{P}$$

ρ is the density of the gas in g/L

1.4 Kinetic Molecular Theory

Postulates of the Kinetic Molecular Theory of Gases:

1. **Small particles (atoms or molecules) in gas move rapidly and randomly.**

   Gas molecules moving in all directions at high speeds cause a gas to fill the entire volume of a container.

2. **The attractive forces between gas particles are negligible.**

   Gas particles move far apart and expand to fill a container of any size and shape.

3. **Gas molecules occupied very small volume compared to the volume that the gas occupies.**

   Most of the volume of a gas is empty space, which allows gases to be compressible.

4. **The average kinetic energy of gas molecules is directly proportional to temperature.**

Gas particles move faster as the temperature increases, hitting the walls of the container with more force and producing higher pressures.

5. **Gas particles move in straight paths until colliding with other gas particles or with the walls of the container to bounce off elastically in other directions.**

An increase in either the frequency or force of collisions lead to an increase in the gas pressure.

Briefly kinetic model is based on three assumptions:

1) The gas exhibits random motion.

2) The size of the molecules is negligible (much smaller than the average distance travelled between collisions).

3) The molecules interact through infrequent and elastic collisions.

$$\overline{v_x^{\,2}} = \overline{v_y^{\,2}} = \overline{v_z^{\,2}} \rightarrow \overline{v^2} = \overline{v_x^{\,2}} + \overline{v_x^{\,2}} + \overline{v_x^{\,2}} = 3\overline{v_x^{\,2}}$$

$$\overline{v_x^{\,2}} = \frac{1}{3}\overline{v^2}$$

$$PV = Nm\overline{v_x^{\,2}} = \frac{1}{3}Nm\overline{v^2} = \frac{2}{3}N(\frac{1}{2}m\overline{v^2})$$

Gas Pressure in the Kinetic Theory: $\overline{KE} = \frac{1}{2}m\overline{v^2}$

$$PV = \frac{1}{3}Nm\overline{v^2} = \frac{1}{3}nM\overline{v^2}$$

P = gas pressure, V=volume
$\overline{v^2}$ = mean square velocity
N = number of gas molecules
n = mole number of gas molecules = N/N_A
N_A = Avogadro's number
m = mass of the gas molecule
M = molar mass of the gas molecule

Conclusion

- Gas particle is sensitively reacted to temperature, volume, pressure and number of mole changes.
- Gas has a specific condition at standard temperature and pressure (STP).
- Gas stoichiometry may relates to other properties of gases.
- Properties of gases can be identify using its mole concentration, density, molar mass.
- The speed of gas molecules can be determine using its kinetic theory of gases

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