CHM 101:
Kinetic theory of matter

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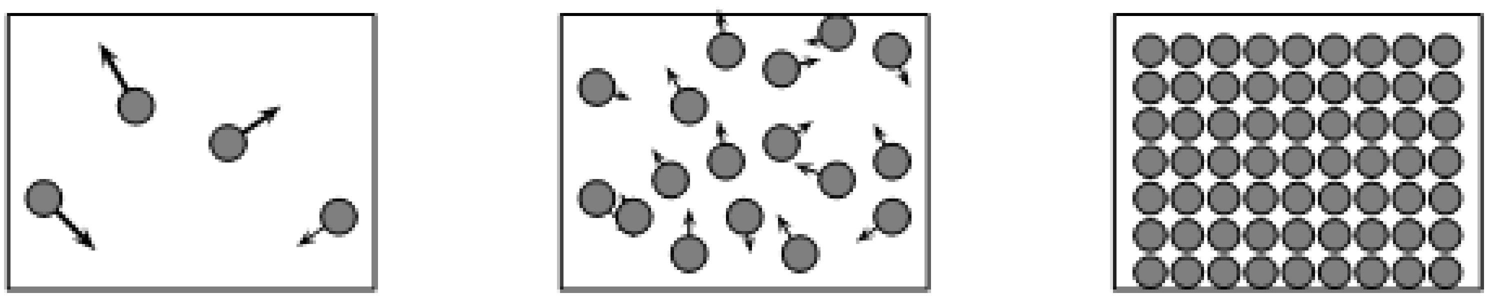
The State of Matter

There are three main kinds of matter: solid, liquids, and gases.



(a) Gas (b) Liquid (c) Solid

Gas **Liquid** **Solid**

Gas properties

-all gases have similar physical properties, and the chemical identity of the substance does not influence those properties.

For example:

all gases **expand** when they are heated in a non-rigid container and **contract** when they are cooled or subjected to increased pressure.

They readily **diffuse** through other gases.

Any quantity of gas will occupy the entire volume of its container, regardless of the size of the container.

Gas pressure

Pressure is defined as the force acting on a unit area of surface, i.e. *force per unit area*.

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

[Force = mass *x* acceleration due to gravity]

$$= \frac{\text{kg ms}^{-2}}{\text{m}^2}$$

$$= \text{Nm}^{-2}$$

$$= \text{Pa}$$

The simplest instrument to measure pressure is Simple barometer.

Units of Pressure

- ✓ The SI unit of pressure is the **Pascal (Pa),**

$$1\ Pa = 1\ N/m^2$$

- ✓ A much larger unit is the **standard atmosphere (atm),** the average atmospheric pressure measured at sea level and 0°C.

$$1\ atm = 1.01325 \times 10^5\ Pa = 101.325\ kPa$$

- ✓ Another unit is bar

$$1\ atm = 1.01325\ bar.$$

- ✓ Another unit is the **millimeter of mercury (mmHg),** which is based on measurement with a barometer or manometer. In honor of Torricelli, this unit has been named the torr:

$$1\ atm = 760\ mmHg = 760\ torr$$

- ✓ Another unit is pounds per square inch ***psi*** (commonly used in Engineering).

$$1\ atm = 14.7\ lb/in^2 = 14.7 psi$$

Exercise 1

Given that the pressure of an unknown gas is 183.45 mmHg.

Convert the pressure to atmospheres, bar, psi, pascal, and torr.

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Exercise 2

a) Convert the following pressure to Pa, torr, mmHg, and atm:

25 psi

42 psi

75 psi

b) Convert the following pressure to psi and atm

250 KPa,	22.7 Pa
230 mmHg,	385 torr

The relationship between Volume and Pressure: Boyle's Law

At constant temperature, the volume of a given sample of a gas is inversely proportional to its pressure.

$$V \propto \frac{1}{P} \qquad \text{(at constant T, n)}$$

This relationship can also be expressed as:

$$PV = \text{constant} \quad \text{or} \quad V = \frac{\text{constant}}{P} \qquad \text{(T \& n fixed)}$$

The relationship between Volume and temperature: Charles's Law

At constant pressure, the volume of a given sample of gas is directly proportional to its ***absolute*** *temperature.*

$V \propto T$ [P, n fixed]

This relationship can also be expressed as:

$\frac{V}{T}$ = constant or V = *constant* X T [P, n fixed]

NOTE: Absolute temperature signifies that the temperature calculations MUST be done in Kelvin scale

[273.15 kelvin = 0^oC]

Other relationships based on Boyle's and Charles's Laws.

1. The combined gas Law:

A simple combination of Boyle's and Charles's laws gives the combined gas law: which applies to situations when two of the three variables (V, P, T) change, hence the effect on the third can be calculated.

$$V \alpha \frac{T}{P} \qquad \text{or} \qquad V = \text{constant} \times \frac{T}{P}$$

$$\frac{PV}{T} = \text{constant}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

2. Pressure – temperature relationships:

At constant volume, the pressure exerted by a fixed amount of gas is directly proportional to the absolute temperature.

$$P \propto T \qquad \text{[V and n fixed]}$$

$$\frac{P}{T} = \text{constant}$$

$$P = \textit{constant} \times T$$

The relationship between Volume and Amount: Avogadro's Law

Avogadro's Law states that the volume occupied by a gas is directly proportional to the amount (mol) of gas (at constant temperature and pressure).

$V \propto n$ [P and T fixed]

$$\frac{V}{n} = \text{constant} \quad \text{or} \quad V = \text{constant} \times n$$

AVOGADRO'S HYPOTHESIS

Avogadro's hypothesis states that *equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.*

Avogadro's hypothesis enables us to determine the relative masses of the molecules (molecular masses) of gases.

The Ideal Gas Law

Each of the gas laws focuses on the effect that changes in one variable have on gas volume:

- ✓ Boyle's Law focuses on pressure ($V \propto 1/P$).
- ✓ Charles's Law focuses on temperature ($V \propto T$)
- ✓ Avogadro's Law focuses on amount (mol) of gas ($V \propto n$).

A combination of these individual effects into one relationship gives Ideal Gas Law (Ideal Gas equation):

$$V \propto \frac{nT}{P} \qquad \text{or} \qquad PV \propto nT \qquad \text{or} \qquad \frac{PV}{nT} = R$$

$$\mathbf{PV = \mathit{n}RT}$$

R is a proportionality constant known as the Universal gas constant AMBASSADOR

Value of R

$$PV = nRT$$

$$R = \frac{PV}{nT}$$

$$= \frac{1\text{atm} \times 22.4141\ \text{L}}{1\ \text{mol} \times 273.15\ \text{K}} = 0.082058\ \frac{\text{atm.L}}{\text{mol.K}}$$

$$\boxed{R = 0.0821\ \text{atm L mol}^{-1}\text{K}^{-1}}$$

$$R = \frac{1.01325 \times 10^{5}\ \text{Pa} \times 22.4141\text{L}}{1\ \text{mol} \times 273.15\ \text{K}}$$

$$\boxed{R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}}$$

The ideal gas law becomes one of the individual gas laws when two of the four variables are kept constant. When initial conditions (subscript $_1$) change to final conditions (subscript $_2$), we have:

$$P_1V_1 = n_1RT_1 \quad \text{and} \quad P_2V_2 = n_2RT_2$$

Thus,

$$\frac{P_1V_1}{n_1T_1} = R \quad \text{and} \quad \frac{P_2V_2}{n_2T_2} = R \quad \text{so} \quad \frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

E.g. when n & T are constant, then:

$$P_1V_1 = P_2V_2 \qquad \text{(Boyles Law)}$$

IDEAL GAS LAW

$$\boxed{PV = nRT \text{ or } (P_1V_1)/(n_1T_1) = (P_2V_2)/(n_2T_2)}$$

fixed
n and T

$$P_1V_1 = P_2V_2$$

Boyle's Law

$$V = \frac{\text{constant}}{P}$$

fixed
n and P

$$V_1/T_1 = V_2/T_2$$

Charles's Law

$$V = \text{constant} \times T$$

fixed
P and T

$$V_1/n_1 = V_2/n_2$$

Avogadro's Law

$$V = \text{constant} \times n$$

Solving Gas Law Problems

Gas law problems are phrased in many ways but they can usually be grouped into 2 main types:

1. A change in one of the four variables causes a change in another, while the two remaining variables remain constant

   [Reduce the Ideal gas law to the specific law needed for the problem solution]

2. One variable is unknown, but the other 3 are known and no change occurs.

   [Apply the ideal gas law ($PV = nRT$) directly]

Exercise 3

Bisola finds that the air trapped in a tube occupies 24.8cm^3 at 1.14atm. By adding mercury to the tube, she increases the pressure of the trapped air to 2.68 atm. Assuming constant temperature, what is the new volume of air (in L)?

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Exercise 4

At what temperature would 3.2 g of helium occupy a volume of 25 L at a pressure of 700 mmHg?

Exercise 5

A gas exerts a pressure of 2.0 atm, at 30°C, in a 10 L container. In what size container would the same amount of gas exert a pressure of 4.0 atm at 20°C?

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Exercise 6

A 0.10 mol sample of oxygen occupies 2.0 L. What volume would be occupied by 0.25 mol of oxygen? Both samples are at the same temperature and pressure.

Exercise 7

Calculate the amount of oxygen gas (O_2) in a cylinder of 30L, if the pressure is 20 atm at 30°C.

The Density of a Gas

One mole of any gas occupies nearly the same volume at a given temperature and pressure, so difference in gas density ($d = m/V$) depend on differences in molar mass.

E.g. 1 mol of O_2 occupies the same volume as 1 mol of N_2, but since each O_2 molecule has a greater mass than each N_2 molecule, O_2 is denser.

All gasses are miscible when thoroughly mixed, but in the absence of mixing, a less dense gas will lie above a more dense one.

The ideal gas law can be used to calculate the density of a gas from its molar mass.

$$n = m/M$$

(n = No. of moles; m = mass; M = molar mass).

Recall $PV = nRT$

Therefore,

$$PV = \frac{mRT}{M}$$

Rearrange $\frac{MP}{RT} = \frac{m}{V}$ = density

This shows that:

1. *The density of a gas is directly proportional to its molar mass* because a given amount of a heavier gas occupies the same volume as that amount of a lighter gas (Avogadro's law)
2. *The density of a gas is inversely proportional to the temperature.* As the volume of a gas increases with temperature (Charles's law), the same mass occupies more space; thus, the density is lower.

Molar mass

To determine the molar mass of an unknown gas:

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

$$M = \frac{mRT}{PV}$$

or

$$M = \frac{dRT}{P}$$

The partial Pressure of a gas

The ideal gas law holds for virtually any gas, whether pure or a mixture, at ordinary conditions for two reasons:

1. Gases mix homogenously (form a solution) in any proportions.
2. Each gas in a mixture behaves as if it were the only gas present (assuming no chemical interactions).

Dalton's law of Partial Pressures: states that *"in a mixture of unreacting gases, the total pressure is the sum of the partial pressures of the individual gases".*

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

E.g. suppose a tank of fixed volume contains gas ***a*** and ***b***. Each gas behaves independently,

$$P_a = \frac{n_a RT}{V} \quad \text{and} \quad P_b = \frac{n_b RT}{V}$$

Each gas occupies the same total volume and is at the same temperature, the pressure of a gas depends on its amount, n.

Thus, the total pressure is:

$$P_{total} = P_a + P_b = \frac{n_aRT}{V} + \frac{n_bRT}{V}$$

$$= \frac{(n_a + n_b)\,RT}{V}$$

$$= \frac{n_{total}\,RT}{V}$$

$$n_{total} = n_a + n_b$$

Each component in a mixture contributes a fraction of the total number of moles in the mixture, which is the mole fraction (X) of that component.

For n_a, the mole fraction is

$$X_a = \frac{n_a}{n_{total}} = \frac{n_a}{n_a + n_b}$$

Since the total pressure is due to the total number of moles, the partial pressure of gas ***a*** is the total pressure multiplied by the mole fraction of ***a***,

$$P_a = X_a \cdot P_{total}$$

Exercise 8

If 4.58 g of a gas occupies 3.33 L at 27^{o}C and 808 torr, what is the molar mass of the gas?

Exercise 9

Calculate the amount of oxygen gas (O_2) in a cylinder of 30 L, if the pressure is 20 atm at 30°C.

Exercise 10

Calculate the absolute temperature of 0.118 mol of a gas that occupies 10.0 L at 0.933 atm.

Exercise 11

What is the pressure of H_2 if 0.250 mol of H_2 and 0.120 mol of He are placed in a 10.0-L vessel at 27^oC.

Graham's Law

Graham's law states that "The rate of effusion or diffusion of a gas is inversely proportional to the square root of its mass".

$$Rate\ of\ effusion\ \ \alpha\ \ \frac{1}{\sqrt{m}}$$

$$Rate\ of\ diffusion\ \ \alpha\ \ \frac{1}{\sqrt{m}}$$

Diffusion is the passage of a gas through another gas. **Effusion** is the process by which a gas escapes from its container through a tiny hole into an evacuated space.

Consider two gases with molar masses M_1 and M_2, The ratio of their rates of diffusion (or effusion) is given by:

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

That is, the heavier a molecule of the gas, the more slowly it diffuses (or effuses).

The rate of effusion or diffusion of a gas is directly proportional to the "average" velocity of its molecules.

Kinetic Molecular Theory

The theory is based on 3 postulates (assumptions):

1. **Particle volume**: A gas consists of a large collection of individual particles. The volume of an individual particle is extremely small compared with volume of the container. In essence the model pictures gas particles having mass but no volume.

2. **Particle motion**: Gas particles are in constant, random, straight-line motion except when they collide with the container walls or with each other.

3. **Particle collisions**: Collisions are elastic, hence their total kinetic energy is constant. Between collisions, the molecules do not influence each other at all.

KINETIC MOLECULAR THEORY (the model)

- ✓Gases are composed of small particles (atoms or molecules).
- ✓These particles move rapidly in a random, straight line motion. Particles will collide with each other and with the walls of the container.

- ✓ The bonding forces between particles are extremely weak. It is assumed that particles move around independently.
- ✓ Collisions between particles are elastic, i.e. energy is conserved.

Kinetic energy (energy of movement) can be transferred from one particle to another, but the total kinetic energy will remain constant.

- ✓ The average kinetic energy of the particles increases as the temperature of the gas is increased.

Exercise 12

A sample of calcium carbonate, mass 1.0 g, is heated until it has decomposed completely. Calculate:

a) the mass of carbon dioxide produced

b) the volume of carbon dioxide, measured at STP

Exercise 13

Copper dispersed in absorbent beds is used to react with oxygen impurities in the ethylene used for producing polyethylene. The beds are regenerated when hot H_2 reduces the metal oxide, forming the pure metal and H_2O. On a laboratory scale, what volume of H_2 at 765 torr and 225^oC is needed to reduce 35.5g of copper (ii) oxide?

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Exercise 14: What is the density of methane, CH_4, at 20°C and 2.00 atm.

Exercise 15: What is the molar mass of a gas whose density at 40°C and 785 torr is 1.286 kg/m^3

Exercise 16: A collapsed balloon and its load weighs 216 kg. To what volume should it be inflated with H gas in order to launch it from a mountain top at -12°C and 628 torr? The density of air under these conditions is 1.11 g/L.

Exercise 17: An organic compound containing 55.8% C, 7.03% H, and 37.2% O was found to have a gas density of 2.83 g/L at 100°C and 740 torr. What is the molecular formula of the compound?

Exercise 18: Chlorine gas is evolved at the anode of a commercial electrolysis cell at the rate of 3.65 L/min, at a temperature of 647°C. On its way to the intake pump it is cooled to 63°C. Calculate the rate of intake to the pump assuming the pressure has remained constant.

Exercise 19: A spark was passed through a 50cm^3 sample of a H_2/O_2 mixture in a gas burette at 18°C and 1.00 atm; the formation of water went to completion. The resulting dry gas had a volume of 10 cm^3 at 18°C, 1.00 atm. What was the initial mole fraction of H in the mixture if:

(a) the residual gas after sparking was H_2

(b) the residual gas was O_2 ?

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Exercise 20: A rigid plastic container holds 35.0g of ethylene gas (C_2H_4) at a pressure of 793 torr. What is the pressure if 5.0g of ethylene is removed at constant temperature?

Exercise 21: A scale model of a blimp rises when it is filled with helium to a volume of 55.0dm^3. When 1.10mol of He is added to the blimp, the volume is 26.2 dm^3. How many more grams of He must be added to make it rise? Assume constant T and P.