Chapter 12: Gases and the Kinetic-Molecular Theory.

In the past chapters, we have been interested in bonding, bonding theories, properties and reactions of certain substances. — ie chemical properties.

We are now beginning a study of <u>physical</u> states. of matter

There are 3 physical states: gas
liquid } fluids — flow freely
solid } condensed states — have much higher densities

Consider the density ($\frac{g}{mL}$ • how much mass per unit volume) of water

	solid	liquid	gas
water	$0.917 \frac{g}{mL}$ (0°C)	$0.998 \frac{g}{mL}$ (20°C)	$0.000588 \frac{g}{mL}$ (100°C)

∴ in 1 mL of ice or liquid water there is ~ 3×10^{22} molecules of H_2O. but in 1 mL of water vapor at 100°C   ~ 2×10^{19} molecules of H_2O. or ~ 1000 × fewer molecules.   ∴ the molecules in vapor are much further apart and can be easily compressed.

Observations on Gases = their MACROSCOPIC behavior. which we will later link to MOLECULAR behavior.
1. gases can be compressed.
2. gases exert pressure on surroundings
3. gases expand without limit
4. gases quickly diffuse into each other and mix
5. gases can be completely described by knowing T, P, volume (V) and the number of molecules or moles of gas present.

Pressure

First let's discuss pressure, P: (force per unit area).

atmospheric pressure is measured with a barometer :
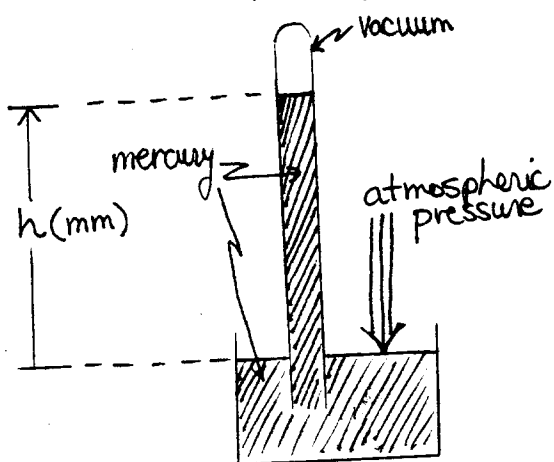
h = height of Hg column (mm)

1 mm Hg = 1 torr

the average sealevel atmospheric pressure = 760 mm Hg = 760
$$= 760 \text{ torr}$$
$$= 1 \text{ atmosphere (atm)}$$
$$= 1 \text{ bar}$$

Note: SI unit of pressure = pascal (Pa)
   1 atm pressure = 1.013×10^5 pascals.
   common unit of pressure is psi (pounds per square inch)
   1 atm pressure = 14.70 psi

Let's consider the relationship between pressure and volume of a gas.

In 1662 , Boyle found that <u>at constant temperature</u>, the volume occupied by a definite mass of gas is inversely proportional to the pressure applied to the gas. This is called <u>BOYLE'S LAW</u>.
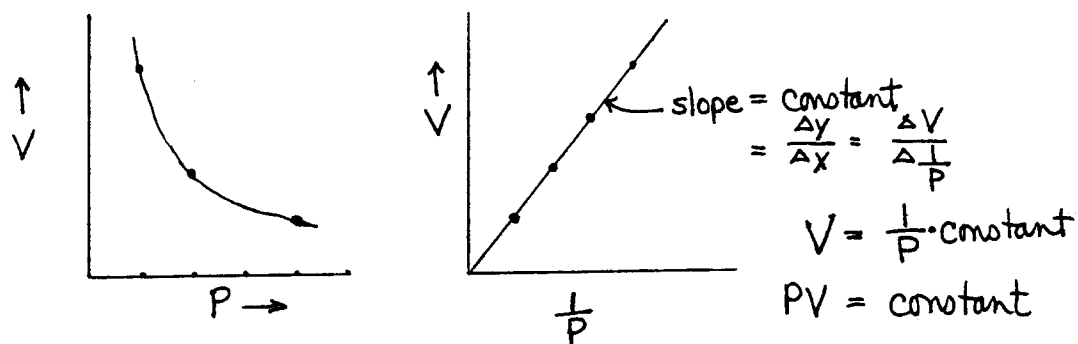
Mathematically, $V \propto \frac{1}{P}$ at constant T, n (number of moles).

   or
   $PV = \text{constant}$ at constant T, n

as pressure increases, the volume decreases at constant T, n

if we double the pressure on a confined gas, the volume of the gas will halve.

Graphically, if we study a sample of gas at constant T and change the pressure + measure the resulting volume:

slope = constant
$$= \frac{\Delta y}{\Delta x} = \frac{\Delta V}{\Delta \frac{1}{P}}$$

$$V = \frac{1}{P} \cdot constant$$

$$PV = constant$$

If we measure P and V for the same sample of gas at the same temperature at two different sets of P and V conditions:

$$P_1 V_1 = constant = P_2 V_2$$

BOYLE'S LAW $\boxed{P_1 V_1 = P_2 V_2 \quad \text{at constant } n, T}$

Example: At 25°C a sample of He occupies 250 mL under a pressure of 760 torr. What volume would it occupy under a pressure of 200 atm at 25°C?

$$P_1 V_1 = P_2 V_2 \quad \text{at constant } n, T \quad^{ok.}$$

recall: 1 atm = 760 torr

∴

$$(1\,atm)(250\,mL) = (2\,atm)\, V_2$$

$$V_2 = \frac{1 \times 250}{2}$$

$$= 125\ mL$$

Example: At 100°C, a sample of O_2 occupies 200 mL under a pressure of 4 atm. Under what pressure would it occupy 800 mL at 100°C?

we know T, number of moles O_2 (n) remain the same. therefore:

$$P_1 V_1 = P_2 V_2$$
$$(4 atm)(200 mL) = P_2 (800 mL)$$

$$P_2 = \frac{4\ atm \times 200\ mL}{800\ mL}$$
$$= 1\ atm$$

Consider a 273 mL volume of a gas at atmospheric pressure and 0°C and change the temperature. How would the volume change?

THEORETICAL ONLY

0 mL   -273°C

1 atm   263 mL   -10°C

1 atm   273 mL   0°C

283 mL   10°C

546 mL   273°C
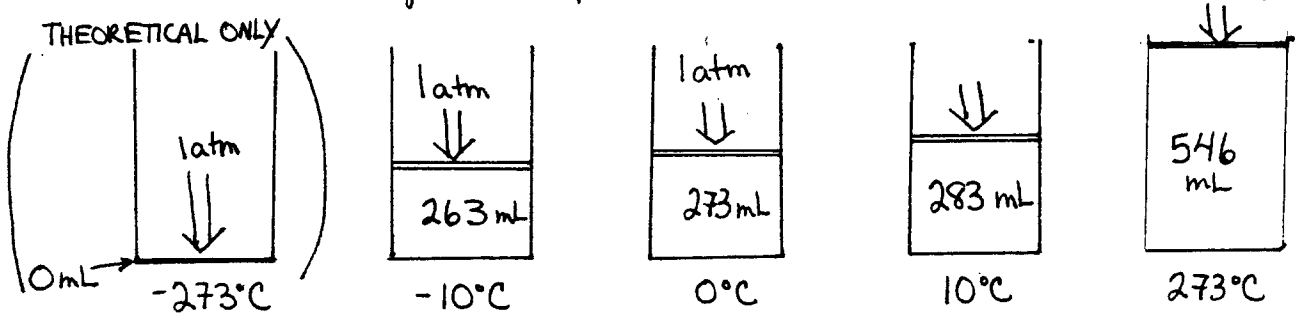
as T increases, V increases
as T decreases, V decreases.
theoretically if T decreased to -273.15°C, V = 0
ABSOLUTE ZERO

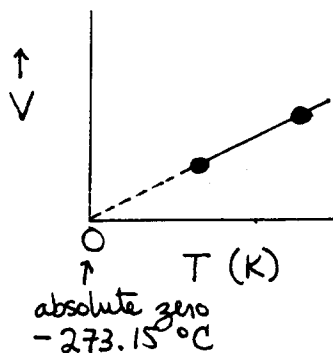we have a new temperature scale, the Kelvin temperature scale,
$$K = °C + 273°$$
named after Lord Kelvin - a British physicist

What we observed is <u>CHARLES LAW</u>: At constant pressure, the volume occupied by a definite mass of gas is directly proportional to its absolute temperature.

$$V \propto absolute\ T \quad at\ constant\ n, P$$
$$\frac{V}{T} = constant$$

graphically, we have

O ↑ T (K)
absolute zero
−273.15 °C

line : $y = mx$
equation
$V = mT$
$\dfrac{V}{T} = constant$

The constant is the same if P and number of moles of gas are the same. for two different situations.

CHARLES' LAW

$$\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2} \qquad constant \ n, P$$

Example: A sample of hydrogen gas, H_2, occupies 100 mL at 25°C and 740 torr. What volume would the gas occupy at 50°C under the same pressure?

we know: P and n are the same ∴ we use Charles' Law.

$$\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2} \qquad at \ constant \ P, n$$

but we must change °C to K
$$T_1 = 25°C = (25 + 273)K = 298 \ K$$
$$T_2 = 50°C = (50 + 273)K = 323 \ K$$

therefore we have
$$\dfrac{100 \ mL}{298 \ K} = \dfrac{V_2}{323 \ K}$$

$$V_2 = 108 \ mL$$

Standard Conditions of Temperature and Pressure

Since volumes of gases vary with both temperature (T) and pressure (P), it is convenient to choose a reference point — some set of standard conditions.

Standard temperature and pressure (STP): $0°C = 273.15 K$
$1 atm = 760 torr$
$(= 101.3 kPa)$

Combined Gas Law

we know $P_1 V_1 = P_2 V_2$ at constant n, T

we also know $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$ at constant n, P

combining, we have:

$$\boxed{\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2} \quad \text{at constant } n}$$

This is the equation I would commit to memory !!

Example: A sample of CO_2 occupies 350 mL at 45°C under a pressure of 910 torr. What volume would it occupy at standard conditions?

recall: standard conditions : 760 torr (= 1 atm) , 0°C (= 273 K)
we are not changing the number of moles of gas ∴ n = constant

$$\dfrac{P_1 V_1}{T_1} = \dfrac{P_2 V_2}{T_2}$$

$T_1 = 45°C$
$= (45 + 273) K$
$= 318 K$

$$\dfrac{910 \text{ torr} \times 350 \text{ mL}}{318 \text{ K}} = \dfrac{760 \text{ torr} \times V_2}{273 \text{ K}}$$

$$V_2 = 360. \text{ mL}$$

We can use the Combined Gas Law in place of Boyle's or Charles' Law calculations.

Example: At 25°C a sample of He occupies 250 mL under a pressure of 760 torr.   What volume would it occupy under a pressure of 2.00 atm at 25°C.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{at constant } n$$

$$\frac{1 \text{ atm} \times 250 \text{ mL}}{298 \text{ K}} = \frac{2 \text{ atm} \times V_2}{298 \text{ K}}$$

since 25°C = (25 + 273) K
= 298 K

$$V_2 = 125 \text{ mL}$$

Standard Molar Volume of Gases

Question : What is the volume of 1 mole of a gas, any gas?

Answer: 1 mole of any <u>ideal</u> gas occupies the same volume at STP. This volume is 22.4 L. (called standard molar volume)

Recall that 1 mole = 6.022×10^{23} molecules.
∴ the same number of molecules of different gases take up the same amount of space at same T and P.

Avogadro's Law $n \propto V$ or $\boxed{\dfrac{V_1}{n_1} = \dfrac{V_2}{n_2}}$ at constant T, P

Real gases do not behave exactly like ideal gases, but under normal conditions, we can use this approximation.
which means :
1 mole Ne or O_2 or H_2 or NO_2 or CH_4 occupies ~ 22.4 L at STP.   (see Table 12-3).

<u>Example</u>: What volume does 42.5 g of N_2 occupy at STP? What is the density of N_2 at STP?

ⓐ we know that 1 mole of gas N_2 occupies 22.4 L at STP

$$\text{at STP,} \quad 22.4 \frac{L}{\text{mole}} = \frac{\# L}{\# \text{moles}}$$

$$\text{moles of } N_2 = \frac{g}{MW} = \frac{42.5 \, g}{280 \, g/\text{mole}} = 1.52 \text{ moles}$$

∴ we have,

$$22.4 \frac{L}{\text{mol}} = \frac{\# L}{1.52 \text{ moles}}$$

$$\# L = 22.4 \frac{L}{\text{mol}} \times 1.52 \text{ mol}$$

$$= 34.0 \, L$$

(b) The density of a gas or liquid $= \frac{\# g}{\# mL}$ (but usually $D_{gas} = \frac{\# g}{\# L}$)

$$= \frac{42.5 \, g}{34 \times 10^3 \, mL}$$

OR more simply
$$D\left(\frac{g}{L}\right) = \frac{MW}{22.4 \, L}$$
$$= \frac{28.0}{22.4 \, L} \, g$$
Assume 1 mol gas
$$= 1.25 \, g/L$$

$$= 1.25 \times 10^{-3} \frac{g}{mL}$$

OR

$$= 1.25 \frac{g}{L} \quad \text{better!}$$

<u>Example</u>: If 2.30 g of a gas occupies 645 mL at STP, what is its molecular weight?

we know at STP $\quad 22.4 \frac{L}{\text{mol}} = \frac{\# L}{\# \text{mole}}$

∴ we can solve for $\# \text{mole} = \frac{\# L}{22.4 \, L/\text{mol}} = \frac{0.645 \, L}{22.4 \, L/\text{mol}}$

$$= 0.0288 \text{ moles}$$

we know molecular weight $= \frac{\# g}{\# \text{moles}}$

$$= \frac{2.30 \, g}{0.0288 \text{ mole}}$$

$$= 79.9 \text{ g/mol}$$

The Ideal Gas Equation:

An <u>ideal gas</u> obeys the gas laws exactly. We work with real gases that show only slight variations.

We have learned that gases can be described in terms of 4 variables.

P pressure   (atm) or (torr = mm Hg)

T temperature   (K)   recall $K = °C + 273$

V volume   (L)

n moles

Boyle's Law $V \propto \frac{1}{P}$ (constant n, T)

Charles' Law $V \propto T$ (constant n, P)

Avogadro's Law $V \propto n$ (constant T, P)

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

OR $PV \propto nT$

IDEAL GAS EQUATION $\boxed{PV = nRT}$ R is proportionality constant called Universal Gas Constant

The value of R depends on units of P

$$R = \frac{PV}{nT}$$ solve at STP

(a) $P = $ atm : $R = \dfrac{1\,atm \times 22.4\,L}{1\,mole \times 273\,K} = 0.0821 \dfrac{atm\,L}{mol\,K}$

(b) $P = $ torr : $R = \dfrac{760\,torr \times 22.4\,L}{1\,mole \times 273\,K} = 62.4 \dfrac{torr\,L}{mol\,K}$

These values of R are on the back of Periodic Table in the exam.

Example: What volume does 48 g of methane occupy at 140°C under a pressure of 1280 torr?

Plan: $g\ CH_4 \xrightarrow{\text{①}} moles\ CH_4 \xrightarrow[\substack{V=\frac{nRT}{P}}]{\text{②}} V.$

(1) $moles\ CH_4 = \dfrac{\#g}{MW} = \dfrac{48g}{16\ g/mol} = 3.0\ mol$

(2) $T = 140°C + 273°C = 413\ K$

$PV = nRT \Rightarrow V = \dfrac{nRT}{P} = \dfrac{3.0\ mol \times 62.4\ \frac{L\cdot torr}{mol\cdot K} \times 413\ K}{1280\ torr} = \underline{60.4\ L}$

Example: A 200. mL flask contains 0.382 g of vapor at 100°C and 736 torr. What is the molecular weight of the compound? (Dumas Method)

Plan: use P, V, T data to solve for n, then solve for $MW = \dfrac{\#g}{\#mol}$

$PV = nRT$

$\therefore n = \dfrac{PV}{RT} = \dfrac{736\ torr \times 0.200\ L}{62.4\ \frac{L\cdot torr}{mol\cdot K} \times 373K} = 0.00632\ moles$

$\therefore MW = \dfrac{\#g}{\#mol} = \dfrac{0.382\ g}{0.00632\ mol} = \underline{60.4\ g/mol}$

Example: What is the density (in g/L) of a sample of carbon dioxide at 150°C and 740 torr?

Derivation of formula: $PV = nRT$ Ideal Gas Law

we also know that $D = \dfrac{\#g}{\#L}$ for gases $\therefore V = \#L = \dfrac{\#g}{D}$

and $n = \dfrac{\#g}{MW}$

substituting in, $P\left(\dfrac{\#g}{D}\right) = \left(\dfrac{\#g}{MW}\right)RT$

cancelling #g, rearranging

$\dfrac{P}{D} = \dfrac{RT}{MW}$

$\boxed{D = \dfrac{MW \times P}{RT}}$

$$\therefore \ D = \frac{MW \times P}{RT} = \frac{44.0 \text{ g/mol} \times 740 \text{ torr}}{62.4 \ \frac{L \cdot torr}{mol \cdot K} \times (150 + 273)K}$$

$$= 1.23 \ \text{g/L}$$

Example: What is the molecular weight of a pure gaseous compound having a density of 2.98 g/L at 73°C and 650 torr?

we know $\quad D = \frac{(MW) \ P}{RT}$

or

$$MW = \frac{DRT}{P}$$

$$= \frac{2.98 \ \text{g/L} \times 62.4 \ \frac{L \cdot torr}{mol \cdot K} \times (73 + 273)K}{650 \ torr}$$

$$= 98.9 \ \frac{g}{mol}$$

The percent composition of this gas is 24 % C, 4 % H and 71 % Cl by mass. What is the molecular formula of the gas?

Assume we have 100 g of gas

$$24. \ g \ C \xrightarrow{\div AW \ (12)} 2 \ mol \ C \xrightarrow{\div 2} 1 \ mol \ C$$
$$4 \ g \ H \xrightarrow{\div AW \ (1)} 4 \ mol \ H \xrightarrow{\div 2} 2 \ mol \ H$$
$$71 \ g \ Cl \xrightarrow{\div AW \ (35)} 2 \ mol \ Cl \xrightarrow{\div 2} 1 \ mol \ Cl$$

$\therefore$ empirical (simplest formula) is CH_2Cl (MW of simplest formula = 49.45

$\therefore$ MW of true formula = MW of empirical formula $\times$ n

$$98.9 \ \cancel{tot} \ \text{g/mol} = 49.45 \ \text{g/mol} \times n$$

$$n = 2$$

$\therefore$ true molecular formula $\bullet$ $(\cancel{CH_2Cl})_2$ or $C_2H_4Cl_2$

Dalton's Law of Partial Pressure

We observe that given a mixture of gases, each gas exerts the pressure that it would occupy if it occupied the volume alone.

Dalton's Law : The pressure of a gas mixture is the sum of the partial pressures of the individual gases : $P_{total} = P_A + P_B + P_C + \cdots$

Example : If 100 mL of H_2, measured at 25°C and 2 atm pressure and 100 mL of O_2, measured at 25°C and 1 atm pressure, were forced into one of the containers at 25°C, what would be the pressure of the gas mixture ?
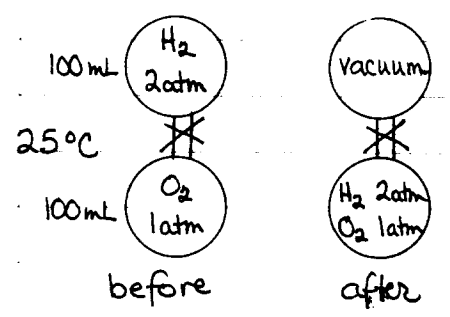
$$P_{total} = P_{H_2} + P_{O_2}$$
$$= 2\,atm + 1\,atm$$
$$= 3\,atm$$

Another way to determine the total pressure of a gaseous mixture is to determine the total number of moles of gas and use the ideal gas equation.

$$n_{total} = n_A + n_B + n_C + \cdots$$

Also,
$$P_A = \frac{n_A}{n_{total}} P_{total}$$

$$P_{total} V = n_{total} RT$$

Example : Calculate the pressure exerted by a mixture of $6.00\,g$ H_2, $12.0\,g$ He and $24.0\,g$ of N_2 in a 20.0 L container at 23°C.

(1) Find n_{total}.

$$n_{total} = n_{H_2} + n_{He} + n_{N_2}$$
$$= \frac{6.00g\ H_2}{2.02g/mol} + \frac{12.0g\ He}{4.00g/mol} + \frac{24.0\ g\ N_2}{28.0\ g/mol}$$
$$= 2.97\ mol\ H_2 + 3.00\ mol\ He + 0.857\ mol\ N_2$$

$$\therefore n_{total} = 6.83 \text{ mol gas}$$

(2) Calculate P_{total} from ideal gas law

$$P_{total} = \frac{n_{total} RT}{V} = \frac{(6.83 \text{ mol})(0.082 L \cdot atm/mol \cdot K)(23°C + 273°)}{20.0 L}$$

$$= 8.30 \text{ atm}$$

Dalton's Law is illustrated in Laboratory Investigation #13 Alka-Seltzer and a Little Gas. CO_2 gas is produced; its volume is measured by displacement of water from a buret.   The leveling bulb is used to make sure the gas is collected at atmospheric pressure (read from a barometer in the lab).
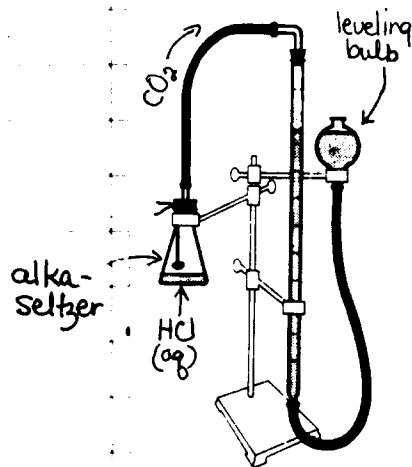
The problem with this means of gas collection is that the pressure inside the buret is the <u>sum</u> of the partial pressure of the gas and the partial pressure of water vapor, P_{H_2O}.

Using the gas laws requires that you use the partial pressure of the gas itself.

Therefore, if the gas is collected at atmospheric pressure,

$$P_{atm} = p_{gas} + P_{H_2O}$$

OR $P_{gas} = P_{atm} - P_{H_2O}$

↗ barometric pressure

↑ from tables of water vapor pressure as a function of temperature.

Example: A sample of O_2 was collected by the displacement of water. The oxygen occupied 427 mL at 27°C when the barometric pressure was 753 torr. The vapor pressure of H_2O at 27°C is 27 torr.

(a) How many grams of O_2 was collected?

(b) What volume would the dry O_2 have at STP?

Any calculation requires knowing the partial pressure of dry O_2.

$$P_{O_2} = P_{atm} - P_{H_2O} = 753 - 27 \text{ torr} = 726 \text{ torr}$$

(a) Plan: $P_{O_2} \xrightarrow[\text{law}]{\overset{\text{ideal}}{\text{gas}}} \text{moles } O_2 \longrightarrow g\ O_2$

$$n = \frac{PV}{RT} = \frac{726 \text{ torr} \times 0.427 L}{62.4 \frac{L \cdot \text{torr}}{\text{mol} \cdot K} (27°C + 273)} = 0.0166 \text{ moles}$$

mass of O_2 = # moles × MW = 0.0166 moles × 32.0 g/mol = 0.530 g

(b) Method I: $P_{O_2} \longrightarrow \text{moles } O_2 \longrightarrow L_{STP}\ O_2$

from (a) we know $n = 0.0166$ moles

$$\therefore V_{STP\ O_2} = 22.4 \frac{L}{\text{mol}} \times 0.0166 \text{ mol} = 0.372 L$$

Method II: Use combined gas law

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

$$\frac{(726 \text{ torr})(427 \text{ mL})}{(27°C + 273)} = \frac{(760 \text{ torr}) V_2}{(273 K)}$$

$$V_2 = 371 \text{ mL}$$

Kinetic Molecular Theory of Gases

Up until now, we have been discussing the observed properties of gases without considering the fact that gases are molecules. Behavior of gaseous molecules should somehow explain the macroscopic properties of gases, such as pressure, volume & temperature.

Bernoulli (1738) proposed that gas molecules were in constant motion, striking the walls of their container and exerting pressure as a result of these collisions.

Clausius (1857) published a theory (Kinetic-Molecular Theory) attempting to summerize observations of Boyle, Charles and Avogadro on a molecular level. The assumptions are given below.

Assumptions of Kinetic-Molecular Theory:

(1) gases consist of discrete molecules that are relatively far apart.
they have little attraction for each other (except near liquifaction point - where gas is turning into a liquid)
volume occupied by gas molecules << total volume occupied by the gas under normal conditions.

(2) gas molecules are in continuous rapid motion with different velocities
they move in straight lines
collisions are elastic (no net transfer of energy)

(3) the average kinetic energy of molecules of gases is directly proportional to the absolute temperature (K).

FIGURE 12-10 The Maxwellian distribution function for molecular speeds. This graph shows the relative numbers of O₂ molecules having a given speed at 25°C and at 1000°C. At 25°C most O₂ molecules have speeds between 200 and 600 m/s. The graph approaches the horizontal axis, but does not reach it; a finite fraction of the molecules have very high speeds.
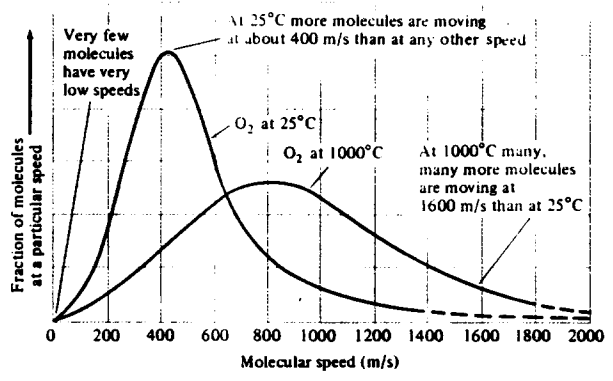
the average kinetic energy of molecules of different gases are equal at a given temperature.

Example: Let us compare the relative velocities of H_2 and CO_2 molecules at any given temperature.

$$KE_{H_2} = KE_{CO_2} \quad \text{at any given temperature}$$

$$\tfrac{1}{2} m_{H_2}(V_{H_2})^2 = \tfrac{1}{2} m_{CO_2}(V_{CO_2})^2 \quad \text{where } m = \text{mass of molecule}$$
$$v = \text{average velocity}$$

$$\tfrac{1}{2}(2 \text{ g/mol})(V_{H_2})^2 = \tfrac{1}{2}(44 \text{ g/mol})(V_{CO_2})^2$$

$$\left(\frac{V_{H_2}}{V_{CO_2}}\right)^2 = \frac{22}{1}$$

$$\frac{V_{H_2}}{V_{CO_2}} = 4.7$$

Therefore, at any given temperature, the lighter molecule, H_2, moves an average of 4.7 times faster than the heavier molecule, CO_2.

Kinetic-Molecular Theory satisfactorily explains most of the observed behavior of gases.

In K.M. theory, the pressure of a gas upon the walls is caused by gas molecules hitting the wall.

∴ P, pressure, is a function of
    (1) number of molecules striking a wall per unit time
    (2) how vigorously they hit the wall.

Boyle's Law: If the volume of gas is halved, molecules will hit the walls twice as often, thereby doubling the pressure.
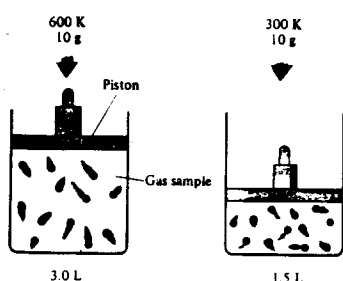
FIGURE 12-11 Molecular interpretation of Boyle's Law—the change in pressure of a gas with changes in volume (temperature constant). The entire apparatus is enclosed in a vacuum. In the smaller volume, more molecules strike the walls per unit time. This gives a higher pressure.
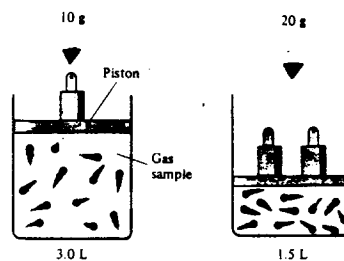
$$P_1 V_1 = P_2 V_2$$

Charles' Law : we know that kinetic energy $\propto$ absolute temperature (K)

if absolute temperature is halved, the kinetic energy of the average molecule is halved also.

there is reduced vigor of collision with the walls and the volume halves.

FIGURE 12-13 Molecular interpretation of Charles' Law—the change in volume of a gas with changes in temperature (pressure constant). At the lower temperature, molecules strike the walls less often and less vigorously. Thus the volume would need to be less to maintain the same pressure.

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

Another observation of gas behavior, as explained by Kinetic-Molecular theory, is a gas' ability to "effuse" through container walls into the atmosphere if the container walls are porous. (has tiny holes). Lighter (lower MW) gases effuse more rapidly than heavier (higher MW) gases through the pores. (because lighter gases move about much faster).

<u>Graham's Law</u> (1832) : Rates of effusion (diffusion) of gases are inversely proportional to square roots of their molecular weights. (or densities)

$$\frac{\text{rate of effusion of A}}{\text{rate of effusion of B}} = \sqrt{\frac{MW_B}{MW_A}}$$

Example : Calculate the rate of effusion of He relative to that of SO_2 under identical conditions.

$$\frac{\text{Effusion rate of He}}{\text{Effusion rate of } SO_2} = \sqrt{\frac{MW \, SO_2}{MW \, He}} = \sqrt{\frac{64}{4}} = \sqrt{16} = 4$$

Therefore He, the lighter smaller molecule, would effuse 4 times faster than SO_2 under identical conditions. Therefore, if 0.1 mol of He effuses thru a tiny hole in 10s, how long would it take for 0.1 mol of SO_2 to effuse thru the same hole under same conditions ? 40 s .

We can use this info to determine MW of unknown gas

Real Gases

At ordinary temperatures and pressures, most real gases behave like ideal gases. They act in accordance with kinetic-molecular theory and obey the ideal gas law.

At high pressures and low temperatures [conditions near where the gas becomes a liquid], significant deviations from ideality can occur and kinetic-molecular theory assumptions break down:

(1) volume occupied by gas molecules themselves is significant

(2) attractions among molecules may become significant.

One way to correct for this is to change the Ideal Gas Law equation somewhat. This new equation is called the Van der Waal's equation.

Ideal Gas Law
$$P_{ideal} \times V_{ideal} = nRT$$

Van der Waal's Equation
$$\left(P_{real} + \frac{n^2 a}{V^2} \right)\left(V_{real} - nb \right) = nRT$$

where $P_{real} < P_{ideal}$, $V_{real} > V_{ideal}$

a, b are empirically derived

(1) "a" corrects for the effect of molecular attraction.
(large attractions correspond to large values of "a")

polar and nonpolar gaseous molecules are attracted to each other to some extent. with London forces and/or dipole-dipole interactions (Ch. 11)

(2) "b" corrects for the actual volume of the gas molecules
(large molecules have large values of "b")

Note: When a, b = 0, the Van der Waal's equation becomes the Ideal Gas Law.

Stoichiometry in Reactions Involving Gases

Recall: Avogadro's Law states $V \propto n$ at constant P, T

at STP, $22.4 \text{ L} = 1$ mole of any ideal gas

Guy-Lussac's Law (Law of Combining Volumes): At constant T and P, the volumes of reacting gases can be expressed as a ratio of simple whole numbers (Again, ONLY TRUE FOR GASES)

Example: $4 NH_{3(g)} + 5 O_{2(g)} \rightarrow 4 NO_{(g)} + 6 H_2O_{(g)}$
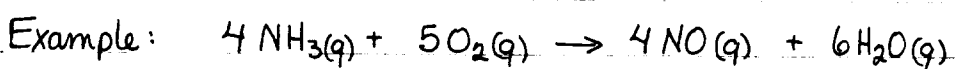
At any given T and P, 4 Liters of $NH_{3(g)}$ will react with 5 liters of $O_{2(g)}$ to produce 4 liters of $NO_{(g)}$ and 6 liters of $H_2O_{(g)}$.

(a) What volume of water vapor is produced by reacting 20 mL of NH_3 with excess oxygen gas if all gases are measured at the same T and P?

$$V_{H_2O} (mL) = V_{NH_3} \times \frac{6}{4} = 20 \text{ mL} \times \frac{6}{4} = 30 \text{ mL}$$

(b) What volume of NO is produced by the reaction of 20 mL NH_3 and 20 mL of O_2, if all gases are measured at the same T and P? (Limiting reagent problem)

$$4 NH_{3}(g) + 5 O_{2}(g) \rightarrow 4 NO (g) + 6 H_2O (g)$$
$$\underset{20 mL}{} \quad \underset{20 mL}{}$$
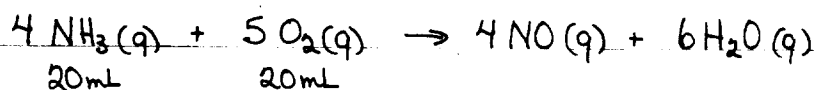
• to find limiting reagent (1) divide mL (or moles) by stoichiometric coefficient
(2) smaller number belongs to limiting reagent.

NH_3: 20 mL ÷ 4 = 5 $\Big\}$ ∴ O_2 is limiting reagent (NH_3 is in excess)
O_2: 20 mL ÷ 5 = 4   and calculations are based on amount of O_2.

$$V_{NO} (mL) = V_{O_2} \times \frac{4}{5} = 20 \text{ mL} \times \frac{4}{5} = 16 \text{ mL}$$

Let us consider: stoichiometric calculations involving both gases + solids.

Example: What volume of pure oxygen gas, O_2, measured at 200 °C and 780 torr, is formed by complete dissociation of 10.0 g of Ag_2O, according to the reaction:

$$2Ag_2O_{(s)} \longrightarrow 4Ag_{(s)} + O_{2(g)}$$
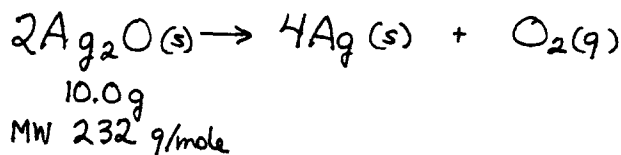
10.0 g
MW 232 g/mole

Plan: g Ag_2O $\xrightarrow{MW}$ moles Ag_2O $\xrightarrow{ratio}$ moles O_2 $\xrightarrow{PV=nRT}$ Volume O_2

(1) # moles Ag_2O = $\dfrac{\text{\# g } Ag_2O}{MW}$ = $\dfrac{10.0\,g}{232\,g/mol}$ = 0.0431 moles

(2) # moles O_2 = # moles $Ag_2O \times \dfrac{1}{2}$ = 0.0216 moles
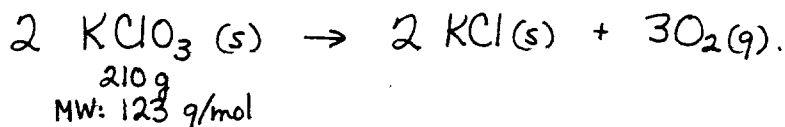
(3) V_{O_2}:

$$PV = nRT$$
$$V = \dfrac{nRT}{P}$$
$$= \dfrac{0.0216 \text{ moles} \times 62.4 \frac{torr \cdot L}{mol \cdot K} \times 473\,K}{780 \text{ torr}}$$

$$= 0.817\ L$$

Example: What volume of oxygen measured at STP can be produced by thermal decomposition of 210 g of $KClO_3$?

$$2\ KClO_{3\,(s)} \longrightarrow 2\ KCl_{(s)} + 3O_{2\,(g)}.$$

210 g
MW: 123 g/mol

Plan: g $KClO_3$ $\rightarrow$ moles $KClO_3$ $\rightarrow$ moles O_2 $\rightarrow$ V_{O_2}

(1) # moles $KClO_3$ = $\dfrac{\text{\# g}}{MW}$ = $\dfrac{210\,g}{123\,g/mol}$ = 1.71 mol $KClO_3$
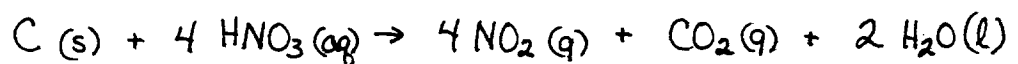
(2) # moles O_2 = # moles $KClO_3 \times \dfrac{3}{2}$ = 2.56 mol O_2

Recall at STP, standard molar volume of any gas $= 22.4 \frac{L}{mol}$

$\therefore \quad 22.4 \frac{L}{mol} = \frac{\# L}{\# mol}$

$V_{O_2} (L) = 22.4 \frac{L}{mol} \times \# mol$

$= 57.4 \, L$

Example: A 25.0 g sample of C(s) reacts with a stoichiometric amount of nitric acid. What is the TOTAL pressure (consider only the gases) of the products if the volume is 3.00 L and the temperature is 95°C?

$$C_{(s)} + 4 \, HNO_{3 \, (aq)} \rightarrow 4 \, NO_2 \, (g) + CO_2 \, (g) + 2 \, H_2O \, (\ell)$$

Plan: find out total number of moles of gaseous products $= n_{total} = (n_{NO_2} + n_{CO_2})$
solve for $P_{total} = P_{NO_2} + P_{CO_2}$

since

$P_{total} V = n_{total} RT$
$(P_{NO_2} + P_{CO_2}) V = (n_{NO_2} + n_{CO_2}) RT$ } corollary of Dalton's Law

(1) moles of $C_{(s)} = \frac{\# g}{AW} = \frac{25.0 g}{12.0 \, g/mol} = 2.08$ moles

$\therefore$ moles NO_2 formed $= 2.08 \times 4 = 8.33$
moles CO_2 formed $= 2.08 \times 1 = 2.08$ } $\therefore n_{total} = 10.41$ moles of gas formed

(2) $P_{total} = \frac{n_{total} RT}{V}$

$= \frac{10.41 \, mol \times 0.0821 \frac{L \, atm}{mol \, K} \times 368 \, K}{3.00 \, L}$

$= 105 \, atm$

Therefore, now we can work with stoichiometric problems when the substances involved are (1) solids, (2) in aqueous solution or (3) gases or combinations of all three.

Remember, in these problems you must work <u>in moles</u> !!

In summary,

(1) solids $\qquad$ # moles = $\dfrac{\text{#g of substance}}{MW}$

(2) in aqueous solution $\qquad$ # moles = $M \times \#L$ $\qquad$ since M, molarity = $\dfrac{\text{#mol}}{\#L}$

(3) gases $\qquad$ # moles = $n = \dfrac{PV}{RT}$ $\qquad$ since $PV = nRT$

$\qquad$ and at STP $\qquad$ $n = \dfrac{\#L}{22.4 \ L/_{mol}}$ $\qquad$ since $22.4 \dfrac{L}{mol} = \dfrac{\#L}{\#mol}$

You should now be able to handle all types of stoichiometric problems for all kinds of substances. These problems include
$\qquad$ (a) simple stoichiometry
$\qquad$ (b) % yield
$\qquad$ (c) limiting reagent