Chapter 5
The Gaseous State

I) Pressure

Pressure is the force exerted per unit area.

A) Devices used to measure pressure

1) barometer
- used to measure the atmospheric pressure
- at seal level and 0 °C, $P_{atm} = 760$ mmHg

2) manometer
- used to measure the pressure of a gas in a laboratory

a) closed end manometer
- mercury filled U-tube
- Δh = gas pressure (P)

b) open-end manometer
- compare pressure of a gas to the atmospheric pressure
- $P_{gas} = P_{atm} + \Delta h$

B) Units of Pressure

SI units: pascal Pa = $Kg/m \cdot s^2$

commonly used units: 1 mmHg = 1 torr
1 atm = 760 mm Hg = 760 torr
1 atm = 1.01325×10^5 Pa
1 atm = 101.325 kPa

II) Empirical Gas Laws

Relationship between volume (V), pressure (P), and temperature (T) of a given amount of gas (moles)

A) Boyle's Law

- relationship between volume and pressure
- at constant temperature and amount of gas

definition: At constant temperature, the volume occupied by a finite mass of gas is *inversely* proportional to the applied pressure.

$V \propto 1/P$ at a given temperature
$PV = \text{constant}$

comparing two sets of V and P at a given temperature

$$\mathbf{P_1V_1 = P_2V_2}$$

Example:
A sample of argon gas occupied 105 mL at 0.871 atm. If the temperature remains constant, what is the volume (in L) at 197 mmHg?

$$P_1V_1 = P_2V_2$$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{(0.871\text{ atm})(105\text{ mL})}{(0.259\text{ atm})}$$

$$V_2 = 353\text{ mL}$$

B) Charles' Law

- relationship between volume and absolute temperature
- at constant pressure and given amount of gas

definition: At constant pressure, the volume of a fixed amount of gas is *directly* proportional to its absolute temperature.

V $\propto$ Tabs at a fixed P and amt. of gas

V/T_{abs} = constant T_{abs} = absolute temp. (Kelvin)

Law expressed in terms of two pairs of variables

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

Example:
A 425 mL sample of fluorine gas is heated from 22 ^{o}C to 185 ^{o}C at constant pressure. What is the final volume?

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

$$V_2 = \frac{V_1T_2}{T_1} = \frac{(425\text{ mL})(458\text{ K})}{(295\text{ K})}$$

$$V_2 = 295\text{ mL}$$

C) Gay-Lussac's Law

- relationship between pressure and absolute temperature
- at constant volume and amount of gas

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

$P \propto T_{abs}$ at fixed V and amt. of gas

P/T_{abs} = constant

for two sets of variables

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

example:
In an autoclave, steam at 100 °C is generated at 1.00 atm. After the autoclave is closed, the steam is heated at constant volume until the pressure gauge indicated 1.13 atm. What is the new temperature in the autoclave?

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

$$P_1 T_2 = P_2 T_1$$

$$T_2 = \frac{P_2 T_1}{P_1} = \frac{(1.13\ \text{atm})(100+273\ \text{K})}{(100\ \text{atm})}$$

$$T_2 = 421\text{K} - 273 = 148^{o}\text{C}$$

D) Combined Gas Law

- expressing Boyle's, Charles', and Gay-Lussac's Laws in 1 statement

PV/T = constant for a given amount of gas

for two sets of data

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

example:
What is the new volume of a sample of oxygen (in L) if 2.75 L at 742 torr and 25.0 °C is heated to 37.0 °C under conditions that let the pressure change to 760 torr?

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

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

$$V_2 = \frac{(742\ \text{torr})(2.75\ \text{L})(310\ \text{K})}{(298\ \text{K})(760\ \text{torr})}$$

$$V_2 = 2.79\ \text{L}$$

Practice:
Divers working from a North Sea drilling platform experiences pressures of 5.0×10^{1} atm at a depth of 5.0×10^{2} m. If a balloon is inflated to a volume of 5.0 L (volume of a lung) at that depth at a water temperature of 4.0 °C, what would the volume of the balloon be on the surface (1.0 atm pressure) at a temperature of 11 °C?

answer: $(2.6 \times 10^2$ L)

E) Avogadro's Law

- relationship between volume and amount of gas
- fixed temperature and pressure

Definition: equal volumes of gas contain an equal number of molecules or moles of gas

$V \propto n$ at constant T, P

n = moles of gas

	$3\ H_2\ (g)$	+	$N_2\ (g)$	→	$2\ NH_3\ (g)$
n:	3 moles		1 mole		2 moles
V:	3 volumes		1 volume		2 volumes

F) Standard Conditions

a set of conditions for basic reference in comparing properties of gases

STP - Standard Temperature and Pressure

T_{std} = O °C (273 K)
P_{std} = 1 atm

At STP, **one mole of a gas occupies a volume of 22.4 L**
The above statement is true for any gas.

Std. molar volume = V_m = 22.4 L/mol

III) Ideal Gas Law

A) Ideal Gas Law equation

- so far we discussed the effects of isolated variables of P, V, T, and n
- now lets combine these relations into one equation

1) Ideal Gas Law

know: $V \propto 1/P$ (Boyle's Law); $V \propto T_{abs}$ (Charles' Law); $V \propto n$ (Avogadro's Law)

combine all three laws into one statement

$V \propto \frac{nT}{P}$ set up equality

$\frac{VP}{nT} = \text{constant} = R$ R is the ideal gas law constant

$PV = nRT$ **Ideal Gas Law**

Ideal gas assumptions:

- molecules that do not attract of repel one another
  (no interactions between molecules)
- volume of a gas molecules is negligible compared to the volume of the container
  (molecules have negligible volumes)

The ideal gas law equation describes a gas fairly well within reasonable conditions: low to moderate pressures and not too low temperatures. This equation breaks down at high pressures and low temperatures.

2) Gas Law constant

What is the value of the gas law constant, R?

- use 1 set of conditions to solve the ideal gas law equation
- 1 mole of gas at STP

$PV = nRT$

$P = 1$ atm; $T = 273$ K; $n = 1$ mole; $V = 22.4$ L

$$R = \frac{PV}{nT} = \frac{(1\ \text{atm})(22.4\ \text{L})}{(1\ \text{mol})(273\ \text{K})} = 0.0821 \frac{\text{atm L}}{\text{mol K}}$$

It is possible to determine a value for R using a different set of units

i.e. using P = 760 mmHg; T = 273 K; n = 1 mole; V = 22.4 L

$$R = \frac{PV}{nT} = \frac{(760\ \text{mmHg})(22.4\ \text{L})}{(1\ \text{mol})(273\ \text{K})} = 62.4\frac{\text{mmHg L}}{\text{mol K}}$$

example:

A tank with fixed volume of 438 L is filled with 0.885 kg O_2. Calculate the pressure of oxygen at 21 °C.

$$PV = nRT$$

$$n = 885\ \text{g}\ O_2\left(\frac{1\ \text{mol}\ O_2}{32.0\ \text{g}\ O_2}\right) = 27.7\ \text{mol}$$

$$P = \frac{nRT}{V} = \frac{(27.7\ \text{mol})\left(0.0821\frac{\text{atm L}}{\text{mol K}}\right)(294\ \text{K})}{438\ \text{L}} = 1.53\ \text{atm}$$

B) Density and the Ideal Gas Law

recall: $d = \frac{m}{V}$

The ideal gas law can be rearranged to give the density.

1) define mole (n)

$$\text{mole} = \frac{\text{mass}}{\text{molar mass}} \Rightarrow n = \frac{m}{M_M}$$

2) substitute n = m/M_m into the ideal gas law

$$PV = nRT = \frac{m}{M_m}RT$$

3) rearrange equation to solve for the density, m/V

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

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

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

example:
Calculate the density of ammonia (NH_3) in grams per liter (g/L) at 752 mmHg and 55 ^oC.

$$d = \frac{m}{V} = \frac{PM_m}{RT} = \frac{(752\text{ mmHg})\left(\frac{1\text{ atm}}{760\text{ mmHg}}\right)\left(17\frac{g}{mol}\right)}{\left(0.0821\frac{\text{atm L}}{\text{mol K}}\right)(328\text{ K})} = 0.624\frac{g}{L}$$

C) Molar mass of an unknown gas

The ideal gas law can be used to find the molar mass of an unknown gas

The ideal gas law can be rearranged to give the density.

1) define mole (n)

$$n = \frac{m}{M_m}$$

2) substitute n = m/M_m into the ideal gas law

$$PV = nRT = \frac{m}{M_m}RT$$

3) rearrange equation to solve for the molar mass, M_m

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

$$M_mPV = mRT$$

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

example:
An organic chemistry isolates a colorless liquid with properties of cyclohexane (Mm = 84.2 g/mol) from a petroleum sample. She obtains the following data to determine molar mass: V = 213 mL, T = 100.0 °C, P = 54 torr, mass of the flask and gas = 78.416 g, mass of flask = 77.834 g. Is the molar mass consistent with the liquid being cyclohexane?

$$P = 754\ \text{torr}\left(\frac{1\ \text{mmHg}}{1\ \text{torr}}\right)\left(\frac{1\ \text{atm}}{760\ \text{mmHg}}\right) = 0.992\ \text{atm}$$
$$T = 100.0\ {}^{o}\text{C} + 273 = 373\ \text{K}$$
$$m = 78.416\ \text{g} - 77.834\ \text{g} = 0.582\ \text{g}$$

$$M_m = \frac{mRT}{PV} = \frac{(0.582\ \text{g})\left(0.0821\frac{\text{atm L}}{\text{mol K}}\right)(373\ \text{K})}{(0.992\ \text{atm})(0.213\ \text{L})} = 84.3\frac{\text{g}}{\text{mol}}$$

D) Stoichiometry problems involving gas volumes

The ideal gas law is useful for calculating the volume of gas from a given amount of gas at specified conditions. Many reactions involve solid or liquid reactants and produce a gaseous product. In these types of reactions it is useful to know the volume of gas produced from a given amount of reactant.

example:
The equation for the metabolic breakdown of glucose is the same as that for the combustion of glucose in air.

$$C_6H_{12}O_6\ (s)\ +\ 6\ O_2\ (g)\ \rightarrow\ 6\ CO_2\ (g)\ +\ 6\ H_2O\ (l)$$

Calculate the volume of CO_2 produced at 37 °C and 1.00 atm when 5.60 g of glucose is used up in the reaction.

First need to calculate the amount of CO_2 produced. Then using the ideal gas law, the moles of gas can be converted into the volume of gas.

$$5.60\ \text{g}\ C_6H_{12}O_6\left(\frac{1\ \text{mol}\ C_6H_{12}O_6}{180\ \text{g}\ C_6H_{12}O_6}\right)\left(\frac{6\ \text{mol}\ CO_2}{1\ \text{mol}\ C_6H_{12}O_6}\right) = 0.187\ \text{mol}\ CO_2$$

PV=nRT

$$V = \frac{nRT}{P} = \frac{(0.187\ \text{mol})\left(0.0821\frac{\text{atm L}}{\text{mol K}}\right)(310\ \text{K})}{(1.00\ \text{atm})} = 4.75\ \text{L}$$

Practice:
A 500.0 mL flask containing a sample of octane, a component of gasoline, is placed in a boiling water bath in Denver, where the atmospheric pressure is 634 mm Hg and water boils at 95.0 °C. The mass of the vapor required to fill the flask is 1.57 g. What is the molecular weight of octane? If the empirical formula is C_4H_9, what is the molecular formula?

IV) Gas Mixtures

A) Dalton's Law of Partial Pressures

In a mixture of unreacting gases, the total pressure is the sum of the partial pressures of the individual gases.

$$P_T = P_A + P_B + P_C + \ldots$$

partial pressure - pressure of the individual gas component in the mixture

Unreacting gases behave independently.
Let's look at a mixture of N_2 and H_2 gases, where the volume and temperature are the same for both gases.

$$P_{N_2} = \frac{n_{N_2}RT}{V} \quad \text{and} \quad P_{H_2} = \frac{n_{H_2}RT}{V}$$

Dalton's Law

$$P_T = P_{N_2} + P_{H_2}$$

Substitute in the partial pressures of N_2 and H_2 gases and simplify

$$P_T = \frac{n_{N_2}RT}{V} + \frac{n_{H_2}RT}{V} = (n_{N_2} + n_{H_2})\frac{RT}{V} = n_T\frac{RT}{V}$$

$$P_T = n_T\frac{RT}{V}$$

It would be useful to have a simple relationship between total pressure of a gas (P_T) and partial pressure of a gas (P_A).

We need to define a new term:

mole fraction (χ)

- each component contributes a fraction of the total number of moles in the mixture
- in general:

$$\chi_A = \frac{n_A}{n_T} = \frac{n_A}{(n_A + n_B + \ldots)}$$

Note: the sum of the mole fractions equals one

$$\chi_A + \chi_B + \ldots = \frac{n_A}{n_T} + \frac{n_B}{n_T} + \ldots = \frac{(n_A + n_B + \ldots)}{n_T} = \frac{n_T}{n_T} = 1$$

$$n_A + n_B + \ldots = n_T$$

The mole fraction will be useful in defining a simple relationship between P_T and P_A.

Set up a ratio of P_A to P_T

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

simplify

$$\frac{P_A}{P_T} = \frac{n_A}{n_T} = \chi_A$$

rearrange

$$P_A = \chi_A P_T$$

relationship between P_T and P_A

B) Collecting gases over water

refer to figure 5.16 in Ebbing

- A gas is bubbled through water which carries some of the water into the vapor phase
- The amount of water vapor depends on the temperature
- Table 5.6 p203 in Ebbing gives a list of P_{H2O} at different temperatures
- vapor pressure of water = partial pressure of water vapor

If gas is collected over water, the vapor pressure of water must be subtracted from the total pressure.

$P_T = P_{gas} + P_{H2O}$

$P_{gas} = P_T - P_{H2O}$

Example:
Oxygen gas generated in the decomposition of potassium chlorate is collected over water. The volume of the gas collected at 24.0 ºC and atmospheric pressure of 762 mmHg is 128 mL. Calculated the mass (in grams) of oxygen gas obtained?

At 24.0 ºC, P_{H2O} = 22.4 mmHg; molar mass of O_2= 32 g/mol

$$P_{O_2} = P_T - P_{H_2O} = 762 \text{ mmHg} - 22.4 \text{ mmHg} = 740 \text{ mmHg}$$

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

$$m = \frac{PVM_m}{RT} = \frac{(740 \text{ mmHg})(0.128 \text{ L})\left(32.0\frac{\text{g}}{\text{mol}}\right)}{\left(62.4\frac{\text{mmHg L}}{\text{mol K}}\right)(297 \text{ K})} = 0.164 \text{ g } O_2$$

Practice:
How many moles of O_2 would be obtained from 1.300 g $KClO_3$?
2 $KClO_3$ (s) → 2 KCl (s) + 3 O_2 (g)
If this amount of O_2 were collected over water at 23 ºC and a total pressure of 745 mmHg, what volume would this gas occupy?

answer: V = 0.406 L

V) Kinetic Molecular Theory

A) Postulated of Kinetic Theory

Kinetic energy: energy in motion

$$\mathrm{KE} = \tfrac{1}{2}\underset{\substack{\nearrow\\ \textbf{mass}}}{m}\underset{\substack{\nwarrow\\ \textbf{speed}}}{u}^2$$

1) Particle Size (postulate 1)

- size of gas particles is negligible compared to average distance between them

2) Particle Motion (postulates 2 - 4)

- molecules are in constant random straight-line motion
  in all directions
  various speeds
- collisions are elastic
  no lost of KE
- molecules do not influence each other
  no forces, attractive or repulsive, between molecules

3) Particle Speed, Temperature, Energy (postulate 5)

- at given temperature, all gases have same average KE
  ↑ T, ↑ molecular KE (Note: ↑ = increase in)

  $T \propto \mathrm{KE} = \tfrac{1}{2}m\bar{u}^2$

B) How theory explains behavior of gas samples

1) Origin of Pressure

molecules collide with the surface; this exerts a force
↑ number of molecules; ↑ number of collisions ∴ ↑ P
(postulates 2-4)

2) Boyle's Law (V α 1/P, const. T)

↑ P; ↑ number of collisions (distance between molecules ↓) ∴ ↓ V
↓ V; ↑ frequency of collisions ∴ ↑ P
gases are compressible due to large spaces between molecules
(postulate 1)

3) Charles' Law (V α T, const. P)

↑ T; ↑ molecular speed, ↑ KE
∴ ↑ frequency of collisions and
energetically creating ↑ internal pressure;
result ↑ V to restore constant P
(postulate 5)

VI) Graham's Law of Diffusion and Effusion

A) Diffusion

- the gradual mixing of molecules of one gas with molecules of another by virtue of their kinetic properties. (movement of one gas through another)

- If molecular speeds are fast, then why does diffusion takes a long time?
  reason: molecules experience numerous collisions

B) Grahams' Law of diffusion

$$\text{rate} \propto \frac{1}{\sqrt{M_m}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_{m2}}{M_{m1}}}$$

r_1, r_2 - diffusion rates of gases 1 and 2

M_{m1}, M_{m2} - molar mass of gases 1 and 2

This law is deduced from Kinetic Theory
two gases at the same Temperature have same KE
Derivation:

$$KE = \tfrac{1}{2}m_1\bar{u}_1^2$$

u - speed of gas molecules
m - mass of gas

$$KE = \tfrac{1}{2}m_2\bar{u}_2^2$$

$$\tfrac{1}{2}m_1\bar{u}_1^2 = \tfrac{1}{2}m_2\bar{u}_2^2$$

multiply both sides by 2

$$m_1\bar{u}_1^2 = m_2\bar{u}_2^2$$

rearrange by gathering common variable

$$\frac{\bar{u}_1^2}{\bar{u}_2^2} = \frac{m_2}{m_1}$$

take square root of both sides

$$\frac{\bar{u}_1}{\bar{u}_2} = \sqrt{\frac{m_2}{m_1}}$$

Graham's Law of diffusion

C) Effusion

process by which gas under pressure escapes one compartment of a container to another by passing through small openings

(process in which a gas flows through a small hole in a container)

- effusion of gas into a vacuum
- rate of effusion of a gas also given by Grahams' Law of diffusion
- lighter gas effuse faster than heavier gases at given T & P

$$\frac{r_1}{r_2} = \sqrt{\frac{M_{m2}}{M_{m1}}}$$

Note:

$$\text{rate} \propto \frac{1}{\text{time}}$$

$$\text{therefore } \frac{r_1}{r_2} = \frac{t_2}{t_1}$$

substituting time into Grahams' Law of diffusion or effusion for rate

$$\frac{t_2}{t_1} = \sqrt{\frac{M_{m2}}{M_{m1}}}$$

Example:

Both H_2 and He have been used as the buoyant gas in blimps. If a small leak were to occur, which gas would effuse more rapidly and by what factor?

M_{He} = 4.00 g/mol M_{H2} = 2.02 g/mol

$$\frac{r_{H_2}}{r_{He}} = \sqrt{\frac{M_{He}}{M_{H_2}}} = \sqrt{\frac{4.00\text{g/mol}}{2.02\text{g/mol}}} = \sqrt{2} = 1.41$$

H_2 effuses 1.41 times faster than He

Practice:

If it takes 1.25 min. for 0.01 mol He to effuse, how long will it take for the same amount of ethane (C_2H_6) to effuse?

answer: t_{C2H6} = 3.42 min.

VII) Real Gases: Deviation from Ideal Behavior

A) Differences between ideal and real gases

1) Ideal gases assume
- no interaction between molecules (either attractive or repulsive)
- volume of molecules is negligibly small compared to container

2) Real gases know
- molecules have a finite molecular volume
- interactions between molecules exist

B) van der Waals Equation

van der Waals (1873)
interpretation of real gas behavior at the molecular level

1) Pressure
- approach of a molecule toward the wall of a container
- intermolecular attractions soften collision impact
- overall effect lowers gas pressures more than expected

$$P_{\text{ideal}} = P_{\text{real}} + \frac{an^2}{V^2}$$

a - proportionality constant
n - number of moles of gas
V - volume of gas

(interaction between molecules depends on frequency that two molecules approach once another)

2) Volume
- volume occupied by a gas
- molecules occupy finite (although small) amount of space
- volume inside the container available to gas molecules is reduced

$$V_{\text{ideal}} = V_{\text{real}} - nb$$

n - number of moles of gas
b - constant

recall ideal gas Law

$PV = nRT$

substitute in van der Waals' corrections for P and V

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

van der Waals' equation

adjusts the P up
to account for the
decreased impact of
collisions by attractive
interactions

adjusts the V down
to include only the
free volume not the
volume of the container
taken up by gas molecules

Table 5.7, page 214 in Ebbing lists van der Waals constants (a & b) for some gases

Example

A quantity of 3.50 mol NH_3 occupied 5.20 L at 47 ^oC. Calculate the pressure of the gas (in atm) using

a) ideal gas Law

b) van der Waals equation

(van der Waals constants are a = 4.17 atm L^2/mol^2 and b = 0.0371 L/mol)

a) $PV = nRT$

$$P = \frac{nRT}{V} = \frac{(3.50\ \text{mol})\left(0.0821\frac{\text{atm L}}{\text{mol K}}\right)(320\text{K})}{5.20\ \text{L}}$$

$$P = 17.68\ \text{atm}$$

b) $$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

$$P = \frac{(3.50\ \text{mol})\left(0.0821\frac{\text{atm L}}{\text{mol K}}\right)(320\ \text{K})}{\left[5.20\ \text{L} - (3.50\ \text{mol})\left(0.0371\frac{\text{L}}{\text{mol}}\right)\right]} - \frac{\left(4.17\frac{\text{atm L}^2}{\text{mol}^2}\right)(3.50\ \text{mol})^2}{(5.20\ \text{L})^2}$$

$$P = 16.25\ \text{atm}$$