Gas Laws Recitation

The Fundamentals of Gas Laws

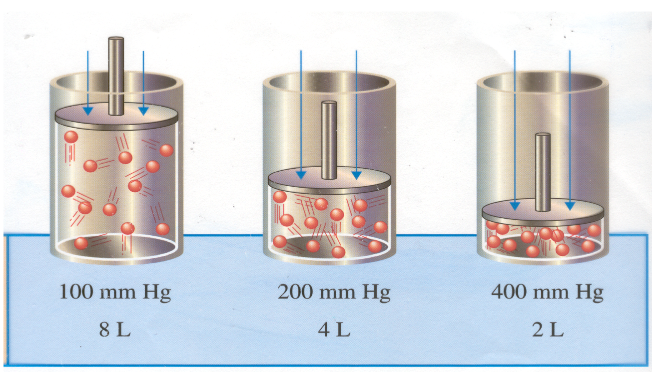
Basic Properties of Gases:

- *Gas volume changes with pressure.*
- *Gas volume changes with temperature.*
- *Gases have a low viscosity.*
- *Low densities (different units are used).* The units for gas densities are reported as g/L while for liquids and solids the densities are reported as g/ml. This is because gases occupy a greater volume and the densities are lower.
- *High miscibility.* The high miscibility is a direct result of the lack of attractive or repulsive forces between molecules in a gas. Gas molecules only interact instantaneously at impact. They have high kinetic energies. The individual molecules or atoms rarely come into contact.

The state of a gases is specified by four variables: pressure, temperature, volume, and the number of moles.

The Relationships Among the Four Parameters

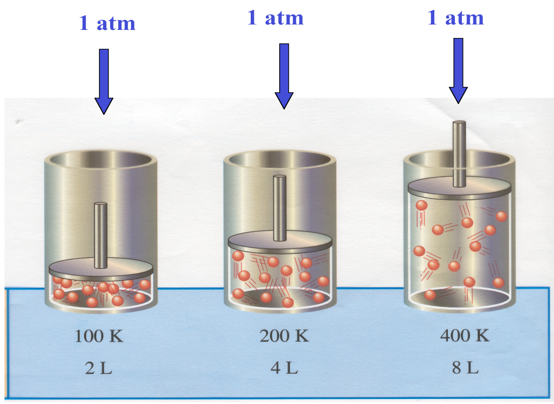
- *Boyle's Law: Says that pressure and volume are inversely proportional when the other parameters are held constant. This is represented as* $V \propto 1/P$ ***or*** $PV =$ ***constant***



A word about proportionality: anytime two parameters are proportional they can readily be represented mathematically using multiplication or division operators. Boyle's Law is often written as $P_1V_1 = P_2V_2$.

- *<u>Charles' Law</u>*: Says that volume and temperature are directly proportional if the other variables are held constant. This is represented mathematically as

  $$\frac{\mathbf{V}}{\mathbf{T}} = \textbf{constant}$$

  The direct proportionality associated with Charles' Law is represented mathematically as $V_1T_2 = V_2T_1$

- *<u>Guy-Lussac's Law:</u>* This law states that pressure and temperature are directly proportional if volume and the number of moles is held constant. Therefore, as with Charles' Law we can derive a similar relationship.

  $P_1T_2 = P_2T_1$

- *<u>Avogadro's Law</u>*: This law defines the relationship between volume and the number of moles. If other variables are held fixed, the volume of a gas is directly related to the number of moles; therefore, regardless of the identity of the gas, whether H_2, N_2, or O_2, one mole will always occupy the same volume. Volume and the number of moles are directly proportional. *An important consequence of Avogadro's work is the relationship that at standard temperature and pressure (273 K, 1 atm), one mole of a perfect gas will occupy exactly 22.4 L.*

Using these variables collectively, the ideal gas law is derived.

$$\left.\begin{array}{l} \mathbf{V \propto 1/P} \\ \\ \mathbf{V \propto T} \\ \\ V \propto n \end{array}\right\} \quad \frac{PV}{nT} = \text{constant}$$

What is the value of this constant? (Assuming STP)

- If P = 1.0 atm
- V = 22.414 L
- n = 1.0 mol
- T = 273.15 K

$$\text{constant} = R = 0.08206 \frac{Latm}{molK}$$

Using the Pascal unit for pressure, we can derive the ENERGY constant R.

- P = 101,325 Pa
- V = 2.24 x 10^{-2} m^3
- n = 1.0 mol
- T = 273 K
- (J = Kg m^2 / s^2)
- (Pa = Kg /m s^2)

$$\text{constant} = R = 8.31 \frac{J}{molK}$$

Overall, the Ideal Gas Law is PV=nRT.

Pressure Conversions

Unit	Atmospheric Pressure	Scientific Field
pascal (Pa); kilopascal (kPa)	1.01325×10^5 Pa; 101.325 kPa	SI unit; physics, chemistry
atmosphere (atm)	1 atm*	Chemistry
millimeters of mercury (mmHg)	760 mmHg*	Chemistry, medicine, biology
torr	760 torr*	Chemistry
pounds per square inch (lb/in^2 or psi)	14.7 lb/in^2	Engineering
bar	1.01325 bar	Meteorology, chemistry, physics

*This is an exact quantity; in calculations, we use as many significant figures as necessary.

Pressure = Force/Area

The units of pressure are N/m^2 where N = 1 kg m/s^2

The nominal unit for pressure is the Pascal. 1 Pascal (Pa) = 1 kg/ms^2

Dalton's Law of Partial Pressure

Because gases are readily miscible, mixtures of gases are very common. We often want to determine the pressure contribution of each gas to the overall pressure of the container. The individual pressure contribution of each gas is known as partial pressure. Therefore, mathematically Dalton's Law is written as:

- $P_{total} = P_1 + P_2 + P_3 + \ldots + P_n$
- P_1, P_2, P_3, etc. are called partial pressures.

At constant temperature and volume, the partial pressures can be rewritten using the ideal gas law.

$$P_1 = n_1\left(\frac{RT}{V}\right) \qquad P_2 = n_2\left(\frac{RT}{V}\right) \qquad P_n = n_n\left(\frac{RT}{V}\right)$$

The partial pressure of each gas is directly related to the number of moles of the gas molecule in the mixture.

With rearrangement of the form above:

$$P_{total} = (n_1 + n_2 + n_3 + \ldots + n_n)\left(\frac{RT}{V}\right)$$

Therefore, we can look at the mole fraction as a way of determining the partial pressure. The mole fraction is determined as follows:

$$X_1 = \frac{n_1}{n_1 + n_2 + n_3 + \ldots + n_n} = \frac{n_1}{n_{total}}$$ Where X_1 represents the fraction of a given gas molecule.

$$\textit{but } \mathrm{n} = \frac{\mathrm{PV}}{\mathrm{RT}} \text{ so using Partial Pressures } \mathrm{P}_1, \mathrm{P}_2, \textit{etc},$$

$$\text{so } \mathrm{X}_1 = \frac{P_1\left(\frac{V}{RT}\right)}{P_{total}\left(\frac{V}{RT}\right)} = \frac{P_1}{P_{total}}$$

Overall to compute the individual partial pressures we can use the following expressions:

$P_1 = X_1 \cdot P_{total}$

$P_2 = X_2 \cdot P_{total}$ etc.

Kinetic Theory of Gases

These are the guiding principles which are used to define the parameters affiliated with gases.

1. A gas consists of tiny particles, either atoms or molecules, moving in random motion.
2. The volume of the particles themselves is negligible compared to the total volume of the gas--most of the volume is empty space.
3. The gas particles are independent of one another--there is no attractive or repulsive forces.
4. Collisions of gases are elastic--either with the walls of the container or with one another; that is, kinetic energy remains constant at constant temperature.
5. The Kinetic Energy of a gas particle is proportional to the temperature (K).

The mathematical relationship between gases and kinetic energy can be approximated using the form:

$$\boxed{\frac{\mathbf{KE_{tot}}}{\mathbf{mol}} = \frac{\mathbf{3}}{\mathbf{2}}\mathbf{RT}}$$

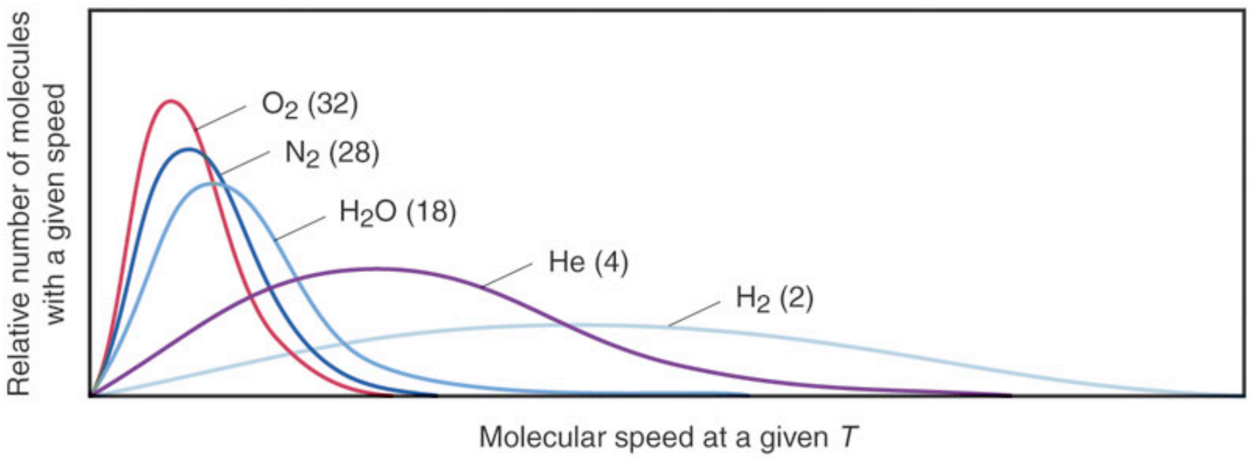
The Kinetic Energy per molecule is therefore equal to: $\frac{KE_{tot}}{molecule} = \frac{3}{2}\frac{RT}{N_A}$

We can determine the average molecular speed using the kinetic energy expression. The physics definition for kinetic energy states that KE=(1/2) mu^2. Therefore, we equate the two expressions to determine the root mean (average) speed for a gas molecule.

$$\frac{KE_{avg}}{particle} = \frac{3}{2}\frac{RT}{N_A} = \frac{1}{2}mu^2 \quad \rightarrow \quad \begin{aligned} \frac{3}{2}\frac{RT}{N_A} &= \frac{1}{2}mu^2 \\ u^2 &= \frac{3}{2}\frac{RT}{N_A}x\frac{2}{m} \end{aligned}$$

$$\begin{aligned} \frac{3}{2}\frac{RT}{N_A} &= \frac{1}{2}mu^2 \\ u^2 &= \frac{3}{2}\frac{RT}{N_A}x\frac{2}{m} = \frac{3RT}{N_A m} = \frac{3RT}{M} \end{aligned} \quad \rightarrow \quad \boxed{u = \sqrt{\frac{3RT}{M}} \quad \text{M should be in used of Kg/mol}}$$

Note that the word average was used. The speeds of gas molecules actually span a wide range of values. The distribution of speeds has a Gaussian shape with a variety of different values. The speed calculated using the equation average represents the average speed. Note the inverse relationship with speed and molecular speed. Larger gas molecules move slower than smaller gas molecules.



Diffusion vs. Effusion

Diffusion - a gas spreads out through another gas to occupy the space uniformly ⇒ mixing of gases by random molecular motion and frequent collisions.

Effusion - a gas flows through a small hole in a container and escapes without collisions

Graham's Law is used to describe the relative rates of effusion:

$$\frac{\textbf{Rate A}}{\textbf{Rate B}} = \frac{\sqrt{\mathbf{M_B}}}{\sqrt{\mathbf{M_A}}} = \sqrt{\frac{\mathbf{M_B}}{\mathbf{M_A}}}$$

Derivation of Graham's Law

$KE = \frac{1}{2} mu^2$

$so\ \mathrm{KE}_{\mathrm{gas\ A}} = \dfrac{1}{2} m_A u_A^2 \text{ and } \mathrm{KE}_{\mathrm{gas\ B}} = \dfrac{1}{2} m_B u_B^2$

Therefore to compare the rate of effusion we set the expressions equal:

$$\frac{1}{2} m_A u_A^2 = \frac{1}{2} m_B u_B^2$$

$u_A = rate$ of effusion for A

$u_B = rate$ of effusion for B

$$\frac{\mathrm{u}_\mathrm{A}^2}{\mathrm{u}_\mathrm{B}^2} = \frac{m_B}{m_A} \quad \text{so} \quad \frac{\mathrm{u}_\mathrm{A}}{\mathrm{u}_\mathrm{B}} = \sqrt{\frac{m_B}{m_A}}$$

Group Exercises and Problems

1. A 2.00-mg sample of argon is confined to a 0.0500-L vial at 20^{o}C; a 2.00-mg sample of Krypton is confined to a different 0.0500-L vial. What must the temperature of krypton be if it is to have the same pressure as Argon?

2. Which is the most dense at 1.00 atm and 298 K: (a.) CO; (b.) CO_2; (c.) H_2S?

   Prove your answer.

3. Calculate the number of molecules in a spherical flask of ammonia with a diameter of 10.0 cm (V = (4/3)pr^3. Assume a pressure of 644 torr and 20^{o}C.

4. A compound used in the manufacture of Saran is 24.7% C, 2.1% H, and 73.2% Cl by mass. The storage of 3.557 g of the compound in a 755-mL vessel at 1^{o}C results in a pressure of 1.10 atm. What is the empirical and molecular formulas for Saran?

5. Dinitrogen oxide, N_2O gas, was generated from the thermal decomposition of ammonium nitrate and collected over water. The wet gas occupied 126 mL at 21^{o}C when the atmospheric pressure was 755 torr. What volume would the same amount of dry nitrogen dixode have occupied if collected at 755 torr and 21^{o}C. The vapor pressure of water is 18.65 torr at 21^{o}C.

6. Determine the density of Argon at STP.

7. Summarize the important points of the Kinetic Theory of Gases.

Individual Problems

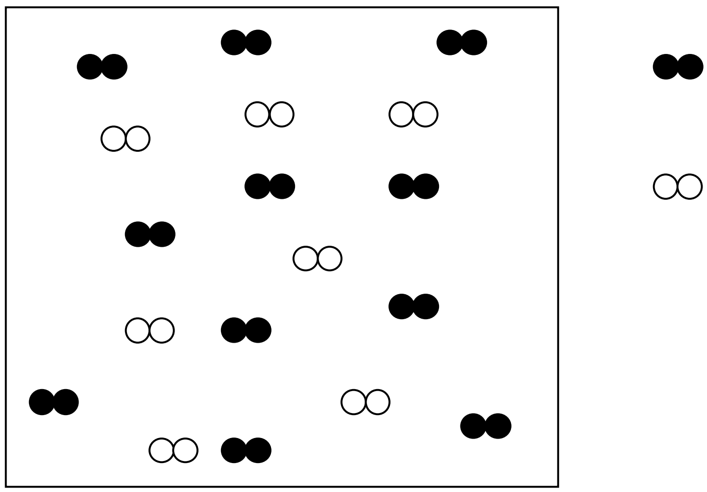
1. How much additional pressure would you need to exert on a sample of helium at 765 torr to compress it from 555 mL to 125 mL at constant temperature?

2. What temperature would be needed to yield the same molecule speed for CO_2 as observed for H_2? Clearly state any assumptions made during this calculation.

3. What is the molecular formula of a compound if the empirical formula is CH and it diffuses 1.25 times more slowly than krypton at the same temperature and pressure?

4. Use the diagram below illustrating the reaction of molecular chlorine and molecular fluorine to form chlorine trifluoride.

$Cl_2\ (g) + 3\ F_2\ (g) \rightarrow 2\ ClF_3\ (g)$



1 mole of fluorine (F_2)

Reaction Conditions: P = 920 torr

T = 120°C

V = 1000 L

a. What are the partial pressures of Cl_2 and F_2 respectively?

b. Which compound F_2 or Cl_2 has a greater average molecular speed? Defend your answer with one sentence.

c. If the pressure is quadrupled using a piston and the volume is cut in half, what happens to the temperature? Show work.

5. Aluminum reacts with EXCESS hydrochloric acid to form aqueous aluminum chloride and 35.8 mL of hydrogen gas over water at 27°C and 1 atm. How many grams of aluminum reacted?

$$2Al\ (s) + 6HCl\ (aq) \rightarrow 2AlCl_3\ (aq) + 3H_2\ (g)$$