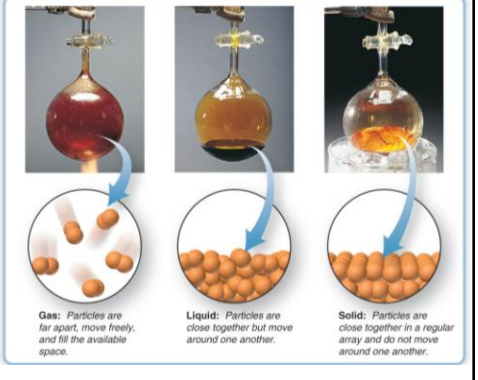
Chapter 5

Gas Laws

5.1 An Overview of the Physical States of Matter

Under appropriate conditions of pressure and temperature most substances can exist as.

- ***Gas*** – conforms to the container shape and fills the entire container.
- ***Liquid*** – conforms to the container shape but fills the container only to the extent of the liquid's volume and forms a surface.
- ***Solid*** – has a fixed shape that does not conform to container shape.



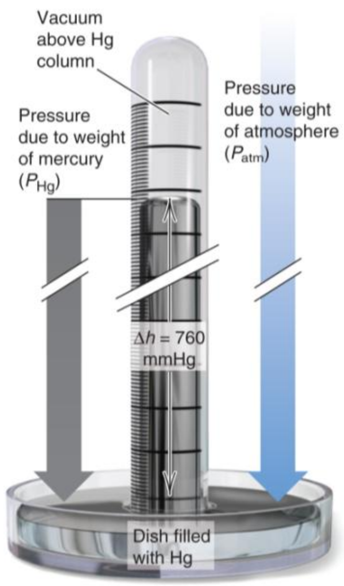
What is unique about a gas? (compared to a liquid and solid)

- Gas volumes change greatly with pressure – that is, gases are *compressible*. Liquids and solids resist significant changes.
- Gas volumes change greatly with temperature.
- Most gases have relatively *low densities* under normal conditions.
- Gases are *miscible* – that is, they mix with one another in any proportion to form a solution.

Measuring Atmospheric Pressure

Chemists have traditionally used two other units of pressure, based on the ***mercury barometer*** – that is, a device for measuring the pressure of the atmosphere invented by Evangelist Torricelli in1643. The height of the mercury in the barometer tube is ~760 mm at sea level.

$$\frac{h_{H2O}}{h_{Hg}} = \frac{d_{Hg}}{d_{H2O}}$$



Units of Pressure

The unit ***millimeters of mercury*** (mmHg) (AKA, the *torr* in honor of Torricelli) is defined as a unit of pressure equal to that exerted by a column of mercury 1 mm high at 0.00°C. The ***atmosphere*** is a unit of pressure equal to exactly 760 mmHg.

1 atm = 760 mmHg

1 atm = 101.325 kPa

$$1 \text{ torr} = 1 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} = 133.322 \text{ Pa}$$

1 bar = 1.0 x 10^2 kPa = 1 x 10^5 Pa

Sample Problem 5.1 Calculate the CO_2 pressure of 291.4 mmHg in torr, atmospheres and kilopascals.

$$P_{CO2}(\text{torr}) = 291.4 \text{ mmHg} \times \frac{1 \text{ torr}}{1 \text{ mmHg}} = 291.4 \text{ torr}$$

$$P_{CO2}(\text{atm}) = 291.4 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} = 0.3834 \text{ atm}$$

$$P_{CO2}(\text{kPa}) = 291.4 \text{ mmHg} \times \frac{1 \text{ atm}}{760 \text{ mmHg}} \times \frac{101.325 \text{ kPa}}{1 \text{ atm}} = 38.85 \text{ kPa}$$

At constant amount and pressure, what will happen to the volume of a gas if the temperature is decreased?

The Gas Laws and their Experimental Foundations

The physical behavior of a sample of gas can be described completely by four variables:

- *Pressure* (P)
- *Volume* (V)
- *Temperature* (T)
- *Amount* (number of moles, *n*)

The variables are interdependent – that is, any one of them can be determined by measuring the other three.

Three key relationships exist among the four gas variables

- *Boyle's Law*
- *Charles's Law*
- *Avogadro's Law*

The individual gas laws are special cases of a unifying relationship called the ***ideal gas law***, which quantitatively describes the behavior of an ***ideal gas*** – one that exhibits linear relationships among volume, pressure, temperature and amount. <u>*No ideal gas actually exists but most simple gases behave nearly ideally at ordinary temperature and pressures.*</u>

Example: Calculating the Volume Occupied by a Gas when Pressure Changes

Boyle's Law tells us that P_iV_i = constant. Therefore, P_fV_f = constant.

$$\frac{P_f V_f}{P_f} = \frac{P_i V_i}{P_f}$$

$$V_f = V_i \times \frac{P_i}{P_f}$$

Suppose you had a 3.15-L sample of neon gas at 21°C and a pressure of 0.951 atm. What would be the volume of this gas if the pressure were increased to 1.292 atm at constant temperature?

Example: Calculating the Volume Occupied by a Gas when Temperature Changes

Charles's Law tells us that V_i/T_i = constant. Therefore, V_f/T_f = constant.

$$T_f \times \frac{V_f}{T_f} = \frac{V_i}{T_i} \times T_f$$

$$V_f = V_i \times \frac{T_f}{T_i}$$

Helium gas, He, at 22°C and 1.00 atm occupied a vessel whose volume was 2.54 L. What volume would this gas occupy if it were cooled to liquid-nitrogen temperature (-197°C)?

Other Relationships Based on Boyle's and Charles's Laws

We can combine Boyle's law (PV = constant) and Charles's law (V/T = constant) into a single equation

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

Example: Calculating the Volume Occupied by a Gas when Temperature and Pressure Changes

$$T_f \times \frac{1}{P_f} \times \frac{P_f V_f}{T_f} = \frac{P_i V_i}{T_i} \times \frac{1}{P_f} \times T_f$$

$$V_f = V_i \times \frac{P_i}{P_f} \times \frac{T_f}{T_i}$$

A bacterial culture isolated from sewage produced 35.5 mL of methane, CH_4 at 31°C and 753 mmHg. What is the volume of this methane at standard temperature and pressure (0°C and 760 mmHg)?

The Relationship between Volume and Amount: Avogadro's Law

Avogadro's law states that equal volumes of any two gases at the same temperature and pressure contain the same number of molecules – that is, one mole of any gas contains the same number of molecules (6.02×10^{23}) and must occupy the same volume at a given temperature and pressure.

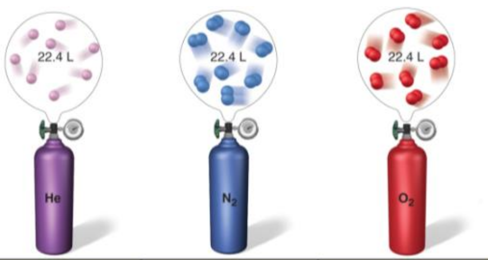
Therefore, at fixed temperature and pressure, the volume occupied by a gas is directly proportional to the amount (moles) of gas:

$V \propto \text{constant} \times n$ OR $\frac{V}{n} = \text{constant}$

Gas Behavior at Standard Conditions

Volumes of gases are often compared at ***Standard Temperature* and *Pressure* (STP)**, which by convention are chosen to be 0°C (273.15 K) and 1 atm pressure (760 torr).

At STP, the volume of one mole (***molar volume***) is found to be 22.4 L.



n = 1 mol	n = 1 mol	n = 1 mol
P = 1 atm (760 torr)	P = 1 atm (760 torr)	P = 1 atm (760 torr)
T = 0°C (273 K)	T = 0°C (273 K)	T = 0°C (273 K)
V = 22.4 L	V = 22.4 L	V = 22.4 L
Number of gas particles = 6.022×10^{23}	Number of gas particles = 6.022×10^{23}	Number of gas particles = 6.022×10^{23}
Mass = 4.003 g	Mass = 28.02 g	Mass = 32.00 g
d = 0.179 g/L	d = 1.25 g/L	d = 1.43 g/L

The Ideal Gas Law

The gas laws (Boyle's, Charles's and Avogadro's) can be combined into one equation, the ***ideal gas law***

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

Where P is the pressure, V is the volume, n is the number of moles, T is the absolute temperature and R is the *universal gas constant*.

N2K	$0.082058 \dfrac{\text{atm L}}{\text{mol K}}$

The ideal gas law is most accurate for low to moderate pressures and for temperatures that are not too low.

A sample of chlorine gas is confined in a 5.00-L container at 328 torr and 37°C. How many moles of gas are in the sample?

5.4 Rearrangements of the Ideal Gas Law

Two Important Equations Derived from the Ideal Gas Law:

$PV = nRT$ Substitute $n = \frac{\text{mass in grams}}{\text{Molar mass}}$

$$PV = \left(\frac{\text{mass in grams}}{\text{Molar mass}}\right) RT$$

Rearrange and solve for Molar mass.

Rearrange and solve for $\frac{\text{mass in grams}}{V}$ - that is, density.

$$\text{Molar mass} = \frac{(\text{mass in grams})\,RT}{PV}$$

$$\text{Density} = \frac{P\,(\text{Molar Mass})}{RT}$$

A 1.23-g sample of a colorless liquid was vaporized in a 250-mL flask at 121°C and 786 mmHg. What is the molar mass of this substance?

Butane, C_4H_{10}, is an easily liquefied gaseous fuel. Calculate the density of butane gas at 0.897 atm and 23°C. Give the answer in grams per liter.

The Partial Pressure of Each Gas in a Mixture of Gases

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

1. Gases are miscible in all proportions.
2. Each gas in a mixture behaves as if it were the only gas present (assuming no chemical interaction).

Dalton's Law of Partial Pressures

The second point above was discovered by John Dalton in his studies of humidity. He discovered that when water vapor is added to dry air, the total air pressure increases by an increment equal to the pressure of the water vapor.

$P_{humid\ air} = P_{dry\ air} + P_{water\ vapor}$

Each gas is observed to exert a ***partial pressure*** – that is, a portion of the total pressure of the mixture that is the same pressure it would exert by itself. In other words,

$P_{total} = P_1 + P_2 + P_3 + \ldots$ **Dalton's Law of Partial Pressures**

Suppose we have a tank that contains nitrogen gas at a certain pressure, P_{N2} , and we introduce a sample of hydrogen gas into the tank. Because each gas behaves independently, we can write for each gas. . .

$$P_{N2} = \frac{n_{N2}RT}{V} \qquad P_{H2} = \frac{n_{H2}RT}{V}$$

The total pressure is simply the sum of the partial pressure of N_2 and the partial pressure of H_2. . .

$$P_{total} = P_{N2} + P_{H2} = \frac{n_{N2}RT}{V} + \frac{n_{H2}RT}{V} = (n_{N2} + n_{H2})\frac{RT}{V} = (n_{total})\frac{RT}{V}$$

Note that each component in the mixture contributes a fraction of the total number of moles in the mixture, which is related to the ***mole fraction*** (X) of that component.

For nitrogen gas in our example, the partial pressure of nitrogen. . .

$$P_{N2} = X_{N2}P_{total}, \text{ where } X_{N2} = \frac{n_{N2}}{n_{total}} \text{ and } P_{total} = (n_{total})\frac{RT}{V}$$

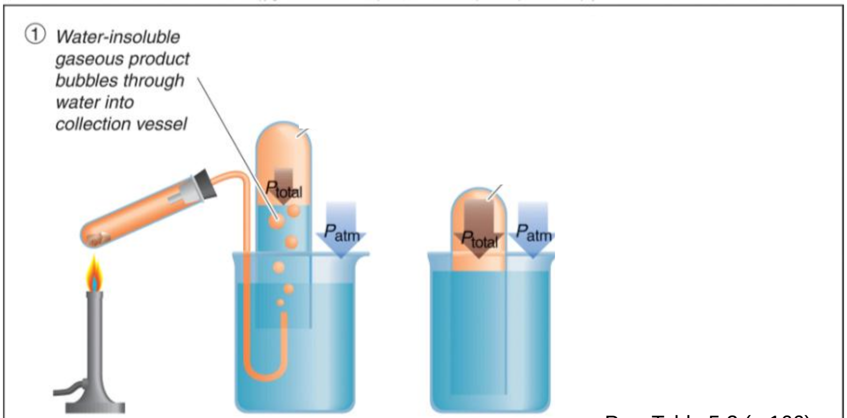
$$= \frac{n_{N2}}{n_{total}}(n_{total})\frac{RT}{V} = \frac{n_{N2}RT}{V}$$

A physiologist prepares an atmosphere consisting of 79 mole % N_2, 17 mole % $^{16}O_2$ and 4.0 mole % $^{18}O_2$. The total pressure is 0.75 atm. Calculate the mole fraction and partial pressure of $^{18}O_2$.

A chemical engineer places 1.37 mole He, 0.743 mole Ne and 0.418 mole Kr in a piston-cylinder assembly at STP (0°C, 1 atm). What is the partial pressure of neon?

Collecting Gas over Water

The law of partial pressures is frequently used to determine the yield of water-insoluble gas formed in a reaction.



P_{H2O} Table 5.2 (p.166)

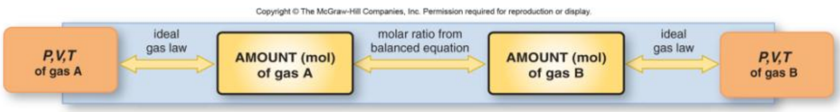
Acetylene (C_2H_2) is produced in the laboratory when calcium carbide (CaC_2) reacts with water:

$$CaC_2\ (s) + 2H_2O\ (l) \rightarrow C_2H_2\ (g) + Ca(OH)_2\ (aq)$$

For the sample of acetylene collected over water, total gas pressure (adjusted to barometric pressure) is 738 torr and the volume is 523 mL. At the temperature of the gas (23°C), the vapor pressure of water is 21 torr. How many grams of acetylene are collected?

The Ideal Gas Law and Reaction Stoichiometry

Here we combine a gas law problem with a stoichiometry problem. It is, in fact, more realistic to measure volume, pressure and temperature of a gas than its mass.



What mass of potassium chloride forms when 5.25 L of chlorine gas at 0.950 atm and 293K reacts with 17.0 g of potassium?

(think limiting reactant/theoretical yield problem)

1. Write a balanced chemical equation: $2K\ (s) + Cl_2\ (g) \rightarrow 2KCl\ (s)$
2. Calculate number of moles of each reactant:

$$n_K = 17.0 \text{ g K} \times \frac{1 \text{ mole K}}{39.10 \text{ g K}} = 0.43478 \text{ mole K}$$

$$n_{Cl2} = \frac{PV}{RT} = \frac{(0.950 \text{ atm})(5.25 \text{ L})}{(0.082058 \text{ atm L/mole K})(293 \text{ K})} = 0.20744 \text{ mole } Cl_2$$

3. Determine theoretical yield from limiting reactant:

$$\text{Moles of KCl (from K)} = 0.43478 \text{ mole K} \times \frac{2 \text{ moles KCl}}{2 \text{ moles K}} = 0.43478 \text{ moles KCl}$$

$$\text{Moles of KCl (from } Cl_2) = 0.20744 \text{ mole } Cl_2 \times \frac{2 \text{ moles KCl}}{1 \text{ moles } Cl_2} = 0.41488 \text{ moles KCl}$$

$$\text{Mass of KCl} = 0.41488 \text{ moles KCl} \times \frac{74.55 \text{ g KCl}}{1 \text{ mole KCl}} = 30.9 \text{ g KCl}$$

How many grams of phosphorus react with 35.5L of O_2 at STP to form tetraphosphorus decaoxide?

$P_4 (s) + 5O_2 (g) \rightarrow P_4O_{10} (s)$

Question you MUST be able to answer:

At 23°C, which molecule will move the fastest – O_2, Ne, N_2, or Ar?

Kinetic Energy and Gas Behavior

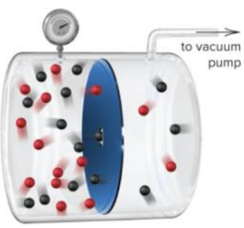
- At a given T, all gases in a sample have the same average kinetic energy.

$$E_k = \frac{1}{2} \text{mass} \times \text{speed}$$

- Kinetic energy depends on both the mass and the speed of a particle.
- At the same T, a heavier gas particle moves more slowly than a lighter one.

Graham's Law of Effusion

- **Effusion** is the process by which a gas escapes through a small hole in its container into an evacuated space.
- **Graham's law of effusion** states that the rate of effusion of a gas is inversely proportional to the square root of its molar mass.
  - A lighter gas moves more quickly and therefore has a higher rate of effusion than a heavier gas at the same T.



$$\text{Rate of effusion} \propto \frac{1}{\sqrt{\mathcal{M}}}$$