

# Chapter 10. Gases

## Common Student Misconceptions

- Students need to be told to *always* use Kelvin in gas problems.
- Students should always use units (and unit factor analysis) in gas-law problems to keep track of required conversions.
- Students often confuse the standard conditions for gas behavior (STP) with the standard conditions in thermodynamics.
- Students commonly confuse effusion and diffusion.

## 10.1 Characteristics of Gases

- All substances have three phases: solid, liquid and gas.
- Substances that are liquids or solids under ordinary conditions may also exist as gases.  
These are often referred to as **vapors**.
- Many of the properties of gases differ from those of solids and liquids:  
Gases are highly compressible and occupy the full volume of their containers.  
When a gas is subjected to pressure, its volume decreases.  
Gases always form homogeneous mixtures with other gases.
- Gases only occupy a small fraction of the total volume of their containers.  
As a result, each molecule of gas behaves largely as though other molecules were absent.

## 10.2 Pressure

- **Pressure** is the force acting on an object per unit area:

$$P = \frac{F}{A}$$

### Atmospheric Pressure and the Barometer

- The SI unit of force is the *Newton* (N).  
 $1 \text{ N} = 1 \text{ kg m/s}^2$
- The SI unit of pressure is the **Pascal** (Pa).  
 $1 \text{ Pa} = 1 \text{ N/m}^2$   
A related unit is the **bar**, which is equal to  $10^5$  Pa.
- Gravity exerts a force on the Earth's atmosphere.  
A column of air  $1 \text{ m}^2$  in cross section extending to the upper atmosphere exerts a force of  $10^5$  N.  
Thus, the pressure of a  $1 \text{ m}^2$  column of air extending to the upper atmosphere is 100 kPa.
  - Atmospheric pressure at sea level is about 100 kPa or 1 bar.
  - The actual atmospheric pressure at a specific location depends on the altitude and the weather conditions.
- Atmospheric pressure is measured with a *barometer*.  
If a tube is completely filled with mercury and then inverted into a container of mercury open to the atmosphere, the mercury will rise 760 mm up the tube.
  - **Standard atmospheric pressure** is the pressure required to support 760 mm of Hg in a column.
  - Important non SI units used to express gas pressure include:
    - **atmospheres** (atm)
    - *millimeters of mercury* (mm Hg) or **torr**
    - $1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa} = 101.325 \text{ kPa}$

### 10.3 The Gas Laws

The equations that express the relationships among  $T$  (temperature),  $P$  (pressure),  $V$  (volume), and  $n$  (number of moles of gas) are known as the *gas laws*.

#### The Pressure-Volume Relationship: Boyle's Law

Weather balloons are used as a practical application of the relationship between pressure and volume of a gas.

- As the weather balloon ascends, the volume increases.
- As the weather balloon gets further from Earth's surface, the atmospheric pressure decreases.

**Boyle's law:** The volume of a fixed quantity of gas, at constant temperature, is inversely proportional to its pressure.

Mathematically:  $V = \text{constant} \times \frac{1}{P}$  or  $PV = \text{constant}$

- A plot of  $V$  versus  $P$  is a hyperbola.
- A plot of  $V$  versus  $1/P$  must be a straight line passing through the origin.

The working of the lungs illustrates that:

- as we breathe in, the diaphragm moves down, and the ribs expand; therefore, the volume of the lungs increases.
- according to Boyle's law, when the volume of the lungs increases, the pressure decreases; therefore, the pressure inside the lungs is less than the atmospheric pressure.
- atmospheric pressure forces air into the lungs until the pressure once again equals atmospheric pressure.
- as we breathe out, the diaphragm moves up and the ribs contract; therefore, the volume of the lungs decreases.
- By Boyle's law, the pressure increases and air is forced out.

#### The Temperature-Volume Relationship: Charles's Law

We know that hot-air balloons expand when they are heated.

**Charles's law:** The volume of a fixed quantity of gas at constant pressure is directly proportional to its absolute temperature.

Mathematically:  $V = \text{constant} \times \frac{1}{T}$  or  $VT = \text{constant}$  (where  $T$  is in K)

- Note that the value of the constant depends on the pressure and the number of moles of gas.
- A plot of  $V$  versus  $T$  is a straight line.
- When  $T$  is measured in  $^{\circ}\text{C}$ , the intercept on the temperature axis is  $-273.15^{\circ}\text{C}$ .
- We define *absolute zero*,  $0\text{ K} = -273.15^{\circ}\text{C}$ .

#### The Quantity-Volume Relationship: Avogadro's Law

- *Gay-Lussac's law of combining volumes:* At a given temperature and pressure the volumes of gases that react with one another are ratios of small whole numbers.
- **Avogadro's hypothesis:** Equal volumes of gases at the same temperature and pressure contain the same number of molecules.
- **Avogadro's law:** The volume of gas at a given temperature and pressure is directly proportional to the number of moles of gas.
  - Mathematically:

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

- We can show that 22.4 L of any gas at 0 °C and 1 atmosphere contains  $6.02 \times 10^{23}$  gas molecules.

## 10.4 The Ideal-Gas Equation

Summarizing the gas laws:

- Boyle:  $V \approx 1/P$  (constant  $n, T$ )
- Charles:  $V \approx T$  (constant  $n, P$ )
- Avogadro:  $V \approx n$  (constant  $P, T$ )
- Combined:  $V \approx nT/P$

**Ideal gas equation:**  $PV = nRT$

- An **ideal gas** is a hypothetical gas whose  $P, V,$  and  $T$  behavior is completely described by the ideal-gas equation.
- $R =$  **gas constant** = 0.08206 L atm/mol K
  - Other numerical values of  $R$  in various units are given in Table 10.2.

Define **STP (standard temperature and pressure)** = 0 °C, 273.15 K, 1 atm.

- The molar volume of 1 mol of an ideal gas at STP is 22.41 L.

### Relating the Ideal-Gas Equation and the Gas Laws

If  $PV = nRT$  and  $n$  and  $T$  are constant, then  $PV$  is constant and we have Boyle's law.

- Other laws can be generated similarly.

In general, if we have a gas under two sets of conditions, then

$$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$$

We often have a situation in which  $P, V,$  and  $T$  all change for a fixed number of moles of gas.

- For this set of circumstances,

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

Which gives

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

## 10.5 Further Applications of the Ideal-Gas Equation

### Gas Densities and Molar Mass

Density has units of mass over volume.

- Rearranging the ideal-gas equation with  $M$  as molar mass we get

$$\frac{n}{V} = \frac{P}{RT}$$

$$\frac{nM}{V} = \frac{PM}{RT}$$

The molar mass of a gas can be determined as follows:

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

$$\therefore d = \frac{PM}{RT}$$

## Volumes of Gases in Chemical Reactions

- The ideal-gas equation relates  $P$ ,  $V$ , and  $T$  to number of moles of gas.
- The  $n$  can then be used in stoichiometric calculations.

## 10.6 Gas Mixtures and Partial Pressures

Since gas molecules are so far apart, we can assume that they behave independently.

Dalton observed:

- The total pressure of a mixture of gases equals the sum of the pressures that each would exert if present alone.
- **Partial pressure** is the pressure exerted by a particular component of a gas mixture.

**Dalton's law of partial pressures:** In a gas mixture the total pressure is given by the sum of partial pressures of each component:

$$P_t = P_1 + P_2 + P_3 + \dots$$

- Each gas obeys the ideal gas equation.
- Thus,

$$P_t = (n_1 + n_2 + n_3 + \dots) \frac{RT}{V} = n_t \frac{RT}{V}$$

### Partial Pressures and Mole Fractions

- Let  $n_1$  be the number of moles of gas 1 exerting a partial pressure  $P_1$ , then
 
$$P_1 = X_1 P_t$$
  - where  $X_1$  is the **mole fraction** ( $n_1/n_t$ ).
  - Note that a mole fraction is a dimensionless (unit-less) number.

### Collecting Gases over Water

- It is common to synthesize gases and collect them by displacing a volume of water.
- To calculate the amount of gas produced, we need to correct for the partial pressure of the water:

$$P_{\text{total}} = P_{\text{gas}} + P_{\text{water}}$$

The vapor pressure of water varies with temperature and values are usually found in Tables (i.e. they are given to you!)

## 10.7 Kinetic-Molecular Theory

The **kinetic-molecular theory** was developed to *explain* gas behavior.

- It is a theory of moving molecules.

**Summary:**

1. Gases consist of a large number of molecules in constant random motion.
2. The combined volume of all the molecules is negligible compared with the volume of the container.
3. Intermolecular forces (forces between gas molecules) are negligible.
  - Energy can be transferred between molecules during collisions, but the average kinetic energy is constant at constant temperature.
4. The collisions are perfectly elastic.
5. The average kinetic energy of the gas molecules is proportional to the absolute temperature.

Kinetic molecular theory gives us an *understanding* of pressure and temperature on the molecular Level:

- a. The pressure of a gas results from the collisions with the walls of the container.
- b. The magnitude of the pressure is determined by how often and how hard the molecules strike.

KEY: The absolute temperature of a gas is a measure of the average kinetic energy.

- Some molecules will have less kinetic energy or more kinetic energy than the **average** (distribution).
  - There is a spread of individual energies of gas molecules in any sample of gas.
  - As the temperature increases, the average kinetic energy of the gas molecules increases.
- As kinetic energy increases, the velocity of the gas molecules increases.
  - **Root-mean-square (rms) speed,  $u$** , is the speed of a gas molecule having average kinetic energy.
- Average kinetic energy,  $\epsilon$ , is related to rms speed:

$$\epsilon = \frac{1}{2} m u^2$$

- where  $m$  = mass of the molecule.

**Application to the Gas-Laws**

We can understand empirical observations of gas properties within the framework of the kinetic-molecular theory.

The effect of an increase in volume (at constant temperature) is as follows:

- As volume increases at constant temperature, the average kinetic energy of the gas remains constant.
- Therefore,  $u$  is constant.
- However, volume increases, so the gas molecules have to travel further to hit the walls of the container.
- Therefore, pressure decreases.

The effect of an increase in temperature (at constant volume) is as follows:

- If temperature increases at constant volume, the average kinetic energy of the gas molecules increases.
- There are more collisions with the container walls.
- Therefore,  $u$  increases.
- The change in momentum in each collision increases (molecules strike harder).
- Therefore, pressure increases.

**10.8 Molecular Effusion and Diffusion**

The average kinetic energy of a gas is related to its mass:

$$KE = \frac{1}{2} m v^2$$

Consider two gases at the same temperature: the lighter gas has a higher rms speed than the heavier gas.

- Mathematically:

$$u = \sqrt{\frac{3RT}{M}}$$

- The lower the molar mass,  $M$ , the higher the rms speed for that gas at a constant temperature.
- Two consequences of the dependence of molecular speeds on mass are:
- **Effusion** is the escape of gas molecules through a tiny hole into an evacuated space.
  - **Diffusion** is the spread of one substance throughout a space or throughout a second substance.

### Graham's Law of Effusion

The rate of effusion can be RELATIVELY quantified.

- Consider two gases with molar masses,  $M_1$  and  $M_2$ , and with effusion rates,  $r_1$  and  $r_2$ , respectively.
  - The *relative* rate of effusion is given by **Graham's law**:

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

- Only those molecules which hit the small hole will escape through it.
- Therefore, the higher the rms speed the more likely it is that a gas molecule will hit the hole.
- We can show

$$\frac{r_1}{r_2} = \frac{u_1}{u_2} = \sqrt{\frac{M_2}{M_1}}$$

### Diffusion and Mean Free Path

Diffusion is faster for light gas molecules.

Diffusion is significantly slower than the rms speed.

- Diffusion is slowed by collisions of gas molecules with one another.
- Consider someone opening a perfume bottle: It takes awhile to detect the odor, but the average speed of the molecules at 25 °C is about 515 m/s (1150 mi/hr).

The average distance traveled by a gas molecule between collisions is called the **mean free path**.

At sea level, the mean free path for air molecules is about  $6 \times 10^{-6}$  cm.

## 10.9 Real Gases: Deviations from Ideal Behavior

From the ideal gas equation:

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

- For 1 mol of an ideal gas,  $PV/RT = 1$  for all pressures.
  - In a real gas,  $PV/RT$  varies from 1 significantly.
  - The higher the pressure the more the deviation from ideal behavior.
- For 1 mol of an ideal gas,  $PV/RT = 1$  for all temperatures.
  - As temperature increases, the gases behave more ideally.

The assumptions in the kinetic-molecular theory show where ideal gas behavior breaks down:

- The molecules of a gas *have* finite volume.
- Molecules of a gas *do* attract each other.

As the pressure on a gas increases, the molecules are forced closer together.

- As the molecules get closer together, the free space in which the molecules can move gets smaller.
- The smaller the container, the more of the total space the gas molecules occupy.
- Therefore, the higher the pressure, the less the gas resembles an ideal gas.
- As the gas molecules get closer together, the intermolecular distances decrease.
- The smaller the distance between gas molecules, the more likely that attractive forces will develop between the molecules.
- Therefore, the less the gas resembles an ideal gas.

As temperature increases, the gas molecules move faster and further apart.

- Also, higher temperatures mean more energy is available to break intermolecular forces.
- As temperature increases, the negative departure from ideal-gas behavior disappears.

### The van der Waals Equation

We add two terms to the ideal gas equation to correct for

- the volume of molecules:  $(V - nb)$

- for molecular attractions:

$$\left( \frac{n^2 a}{V^2} \right)$$

- The correction terms generate the **van der Waals equation**:

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

- where  $a$  and  $b$  are empirical constants that differ for each gas.
- van der Waals constants for some common gases can be found in Table 10.3.

To understand the effect of intermolecular forces on pressure, consider a molecule that is about to strike the wall of the container.

- The striking molecule is attracted by neighboring molecules.
- Therefore, the impact on the wall is lessened.