Chapter Twelve: Gases

Pressure
- An important parameter which must be taken into account when studying gases is pressure.
- Pressure is the amount of force applied to an area:
  \[
  \text{pressure} = \frac{\text{force}}{\text{area}}
  \]
- Consider laying on a bed of nails. Do you want there to be many nails or few nails in the bed?

Pressures of Gases
- The pressure exerted by a gas in a sealed container results from collisions of many individual gas particles with the walls of its container.
  - When we say a gas is at high pressure, its individual particles are colliding frequently with the sides of its container.
- Later we will see that many other parameters can have an effect on the pressure of a gas sample, such as the volume of the enclosing container.

Air Pressure
- The air in the atmosphere exerts a substantial amount of pressure on everything on the surface of the earth.
- Since air is composed of matter (nitrogen, oxygen, etc.), it has mass.
- Air reaches up to at least 20 miles above the surface of Earth.
- The weight of the air pushes down on everything on the surface, including us.
- In a similar fashion, the weight of ocean water exerts tremendous pressures at the lower depths of the oceans.

Measuring Pressure
- A device used for measuring pressure is called a manometer; a device specifically designed to measure air pressure is called a barometer.
- To build a simple barometer, we completely fill a thin cylinder with mercury
  - Mercury is very dense and is therefore ideal for this application
- Then, we partially fill a deep dish with mercury and invert the mercury tube in this pool of mercury.
- Some of the mercury will descend out of the tube as gravity pulls it down.
- However, some of the mercury will stay in the tube, as the air pressure keeps this mercury supported.
  - The weight of the air on the surface of the mercury pool opposes the force of gravity as it tries to pull the mercury down out of the column.
- On an “average” day, the height of the mercury column will be close to 760 mm.
- What would the height of the column be on average at a higher altitude: greater than 760 mm, or less?

- The “standard” air pressure is set at this value of 760 mm, as we shall shortly see.
# Units of Pressure
- Unfortunately, many different units are used to measure pressure.
- The units we will employ most often include
  - Atmospheres (atm)
    - Though not the SI unit of pressure, this is a very common unit. The value of the air pressure at sea level on an average day is close to 1 atm.
  - Millimeters of Mercury (mm Hg)
    - This unit is derived from the way one takes a measurement with a barometer or manometer. Recall that on an average day, the height of a mercury column in a barometer is about 760 mm Hg.
    - 1 atm = 760 mm Hg (approximately, though treat this as exact).
  - Torr (torr)
    - This unit is essentially the same as the mm Hg, so
    - 1 atm = 760 torr (exactly).
- You must know these units and conversions.
- Other units of pressure you may encounter, but need not memorize the conversion for, include
  - Pascals (Pa) (the SI unit of pressure) and kilopascals (kPa)
  - Pounds per square inch (psi)
  - Bars (bar) and millibars (mbar)

\[ 1 \text{ atm} = 101,325 \text{ Pa} = 14.7 \text{ psi} = 1013 \text{ mbar} \]

# Kinetic-Molecular Theory
- Recall that our only previous description of gases stated that gases completely fill and take the shape of their containers.
- The Kinetic-Molecular Theory goes much farther in describing how gases ideally behave.
- There are five principle statements that comprise it, which should be understood thoroughly as well as memorized.
  - Note that some textbooks give slight modifications of these

**The Statements of the Kinetic-Molecular Theory**
- The particles of a gas are so small compared to the distances between them that the volume of the individual gas particles is considered negligible (zero).
- Gas particles are in constant, rapid, and random motion.
- Gas particles exert neither attractive nor repulsive forces on each other.
- The average kinetic energy of a collection of gas particles is directly proportional to the temperature (in Kelvin) of the gas.
  - From this we can state that all gases at the same temperature have the same average kinetic energy.
- Collisions between gas particles are perfectly elastic
  - By this, we mean that the gas molecules do not lose energy when they collide

# The Gas Laws
- In considering gases, there are three important measured values which we will often consider.
  - Pressure (P)
  - Volume (V)
  - Temperature (T)
    - Note that the units of temperature will always be expressed in Kelvin in the gas laws.
- The gas laws describe the mathematical relationship between these parameters
Boyle’s Law
- Suppose we have a gas in a sealed piston (a container whose volume can change), and we know its pressure, volume, and temperature.
- Keeping the temperature the same, we decrease the volume of the container.
- What will happen to the pressure?
  - Hint: Will the gas molecules collide with the sides of the container more or less frequently?

Pressure and volume are inversely proportional.
- That is, if one increases, the other must decrease.
- Remember that the temperature must remain constant for this to be true.
- We can use this fact to derive Boyle’s Law:

\[ P_1 V_1 = P_2 V_2 \] (at constant T)

where the 1 stands for the beginning values and the 2 the final values.

Example
A gas occupies 29.5 L, and exerts a pressure of 640. mm Hg. If the container’s volume is expanded to 40.0 L (keeping the temperature constant), what will be the pressure of the gas in mm Hg and in atm?

Charles’ Law
- Suppose we have a gas in an expandable container, and, without changing its pressure, we raise its temperature.
- How will the behavior of the gas molecules change?

- In order to keep the pressure constant, what will happen to the volume of the gas?
Volume and temperature are directly proportional.
- That is, if one increases the other increases.
- Pressure must remain constant for the process.
Mathematically, this is stated as

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{(constant } P)\]

**Example**
A gas occupies 35.8 L at 1.13 atm and 42.3 °C. What would be the temperature of this gas, in Celcius, if the volume were decreased to 25.0 L and the pressure was left unchanged?

**The Combined Gas Law**
The three previous laws can all be combined into one convenient form, the combined gas law.

\[
\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}
\]

You may use this law in place of the other three if you wish, since the constant values will always divide out.

**Example**
72.6 L of a gas at 35.7 °C and 0.872 atm is heated to 50.0 °C and allowed to expand to 87.5 L. What is the pressure of the gas under these new conditions?
Avogadro’s Hypothesis
- Amadeo Avogadro is credited with stating one of the most fundamental statements describing gases:
  
  “Equal amounts (moles) of gases occupy equal volumes under the same conditions”

- This greatly simplifies our treatment of gases, as we can conclude that, regardless of what composes the gas, if we know how many moles of it we have and its conditions, we can find its volume.

The Ideal Gas Law
- All the previous laws allow us to compare a gas under one set of conditions with its values under other conditions.
- The Ideal Gas Law summarizes the previous laws in a fundamentally different way: its power is that it shows how the four parameters (P, V, T, and n) can be used to determine one another.
- The Ideal Gas Law is, mathematically,

\[ PV = nRT \]

where \( n \) is the number of moles of gas and \( R \) is a constant, called the universal gas constant.

\[ R = 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \]

- If you know any three parameters from the ideal gas law, the fourth can be determined by substitution into this equation.

Examples

What volume is one mole of a gas expected to occupy at exactly 1 atm and exactly 0 °C?

Note: These pressures and temperatures are called STP (standard temperature and pressure).

If a balloon containing methane has a volume of 7.25 L at 754 mm Hg and 296.4 K, then how many moles of methane does the balloon contain? How many grams is this?
**Dalton's Law of Partial Pressures**

- In a mixture of gases (like air) each substance in the mixture exerts its own individual pressure, called the *partial pressure* of that gas.
- The total pressure of the mixture of these gases is simply the sum of these partial pressures.
  - So, air pressure is derived from the partial pressures of all the gases making up the air, including \( \text{N}_2 \), \( \text{O}_2 \), Ar, \( \text{H}_2\text{O} \), \( \text{CO}_2 \), and others.
- Mathematically, this is stated as
  \[
P_{\text{total}} = P_{\text{gas } a} + P_{\text{gas } b} + P_{\text{gas } c} + \ldots
\]
  - There are as many terms on the right side of the equation as there are gases in the mixture.

**Example**

Argon, neon, and helium gases are all combined in a 40.0 L container. The total pressure of the three gases is measured to be 1.45 atm. Argon and neon each exert a partial pressure of 0.65 atm. What is the partial pressure of helium in this mixture?

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**Gas Stoichiometry**

- The Ideal Gas Law aids us in predicting the quantity relationships when reactants or products are gases.
- An important value to keep in mind is that 1 mole of a gas at STP will occupy 22.4 liters.
- We will use the Ideal Gas Law for similar calculations under different conditions.

**Examples**

54.8 L of hydrogen gas is combined with excess oxygen at STP. What mass of water should be produced?
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72.9 L of hydrogen (at STP) is reacted with excess nitrogen, producing ammonia. What volume will the ammonia produced occupy at 1.25 atm and 325 K?

Changes of State

Terms of Change of State:

Solid  Liquid  Gas

Intermolecular Forces

- The attractive forces which exist between different molecules are called intermolecular forces.
- There are three distinct forces we will consider, each with a range of strength
  - Hydrogen Bonding
  - Dipole-Dipole Forces
  - London Dispersion Forces

Hydrogen Bonding

- When hydrogen atoms are bonded to very electronegative atoms, they develop a partially positive charge since the electrons are pulled away from the atom.
- The lone pairs on an electronegative atom of a different molecule will be attracted to this partial positive charge, making a hydrogen bond.

Hydrogen Bonding

- Hydrogen atoms that are covalently bonded to F, O, and N atoms only may participate in hydrogen bonding.
- Similarly, the lone pairs on a F, O, or N atom of another molecule may participate in hydrogen bonding.
- There are no exceptions to this.
- Do not confuse a covalent bond with hydrogen with a hydrogen bond! Covalent bonds share electrons between atoms in the same molecule; hydrogen bonds are attractions between different molecules (for the purpose of this course.)
Examples
- Show how water molecules can hydrogen bond with each other.

- Show how water and ammonia can hydrogen bond together.

- Which of these compounds can hydrogen bond with water?
  
  \[
  \text{CH}_4 \quad \text{CH}_3\text{NH}_2 \quad \text{CH}_2\text{O} \quad \text{HF} \quad \text{NH}_4\text{Cl}
  \]

Hydrogen Bonding and Solubility
- In deciding whether or not certain substances dissolve in each other, chemists have a saying they use: “Like dissolves like.”
- As a general rule, if a compound can make hydrogen bonds, it is likely to be somewhat soluble in water.
- The more sites a molecule can use to make hydrogen bonds, the more soluble it is likely to be.

Example
Explain why the sugar glucose dissolves in water.

![Glucose structure](image)
Dipole-Dipole Forces
- Generally weaker than hydrogen bonds, dipole-dipole forces are the attractions between the positive region of one molecule with the negative regions of another.
- For molecules to engage in this form of attraction, the molecules must have a dipole moment.
- Examples of molecules with dipole-dipole forces are CH₃Cl, H₂S, and ICl.

Van der Waals Forces
- Van der Waals forces (also called London Dispersion Forces) are the weakest of the intermolecular forces.
- Even nonpolar molecules can have a temporary, induced dipole moment as the electrons move over the molecule.
- The positive side of this temporary dipole will be attracted to the negative pole of another molecule.
- This attraction disappears when the temporary dipole reverses itself.

Comparing Intermolecular Forces
- The general order of the strength of intermolecular forces, from strongest to weakest, is Hydrogen Bonding > Dipole-Dipole > van Der Waals
- In comparing intermolecular forces, we generally consider only the strongest force present, as many molecules will display more than one of these forces.

Examples
Which intermolecular force is most significant in for each of the following molecules?

NH₃, CH₃CH₃, Br₂, CHF₃

Important: Always draw the Lewis Structure before answering questions of this type!