7. Gases, Liquids, and Solids
7.1 Kinetic Molecular Theory of Matter

Kinetic Molecular Theory of Matter

The Kinetic Molecular Theory of Matter is a concept that basically states that matter is composed of a very large number of very tiny particles molecules or ions. These particles are constantly in motion and possess energy of motion (kinetic energy) that we perceive as temperature. As the temperature decreased, the molecules of a gas can be condensed to liquids and then to solids. Slowly moving molecules are attracted to each other easily and results in condensed phases: liquid and solids. Ionic compounds never exist as gases since very high temperature is required in overcoming strong electrostatic attraction between the ions. The physical state of a compound is determined by the temperature and the kinetic energy as well as the intermolecular forces in the substance.

intermolecular forces: The forces that are other than chemical bonds that tend to attract two molecules to each other discussed in more detail later in section 7.13 (Three types: 1) hydrogen bonding, 2) dipole-dipole attraction, 3) Londodn dispersion forces).

7.2 Kinetic Molecular Theory and Physical States

Gaseous State:

Gas has high speed molecules

From the Kinetics Molecular Theory of Matter and the Theory of Heat, it follows that molecules are in constant motion. They only stop moving only when temperature reaches **Absolute Zero, 0 K**. **Intermolecular attractions** or forces are always present between molecules. However, the greater large kinetic energy present in a gas is much more than the Intermolecular attractive force between them. Thus, a gas will easily spread to space given to it and not stay in an open container and described by following characteristics:

1. Any gas is composed of a very large number of molecules move in straight lines; their direction is random.
2. Molecules are small. (The volume they occupy is small compared to the total V.)
3. Molecules do not attract or repel each other (**no intermolecular forces**).
4. Elastic collisions i.e., they take place within a negligible span of time and does not lose kinetic energy.
5. Average kinetic energy is proportional to T (K, Kelvin).

Liquid State:

Liquids have slower molecules which roll over each other

When the gas is cooled sufficiently that the molecules have less kinetic energy and are moving slower, the intermolecular forces take over and molecules are attracted each other. This mild binding force holds the material together in the form of a liquid state with following characteristic:.

1. Consists of closely packed particles in continuous, random motion while maintaining the volume.
2. Volume of the liquid is dependent on the size of the particles and effects the properties of a liquid.
3. Slow motion and kinetic energy of the particles allows the **Intermolecular forces** to be present and significantly affect the properties of the liquid.
4. Liquids have fixed volume but take and the shape of container and gravity pulls them down to the bottom.

Solid State:

Molecules in solids can only vibrate

If a liquid is cooled even more, the molecule slow down so much that they get stuck in the structure of a solid. They are not moving freely about. Instead, most of them are simply vibrating in place and have following characteristics:

1. Consists of closely packed particles in vibration in fixed locations while maintaining the fixed volume and shape.
2. Volume of the solid is dependent on the size of the particles and effect on their properties.
3. **Intermolecular forces have stronger effect** on the properties because of the slow vibrations almost no kinetic energy of the particles.
4. Solids have fixed volume and shape and gravity pulls them down to the bottom og the container.

7.3 Gas Law Variables

Measurement of Gases Properties

Following measurements are used to characterize properties of a gas: volume, pressure, temperature and amount.

Volume (V): Gases takes up the volume of the container they occupy. Unit of volume is liter (**L**).

Pressure (P): Gases exert a pressure on the walls of the container because of the collision of molecules with the wall. Unit of pressure is **mm Hg** (**torr**) or **atm**.

1 atm =760 mm Hg or torr.
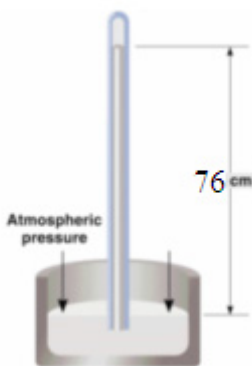
Since the mercury barometer was the first one invented to measure pressure, atmospheric pressure is often expressed in terms of the height of the mercury in the tube above the mercury in the dish. At sea level, this height averages about 30 inches (**760 millimeters**). It varies with the elevation and it would be about 133/4 inches (350 millimeters); and at 30,000 feet (9,000 meters. The changes in atmospheric pressure caused by the weather are much smaller. At sea level weather changes will cause the air pressure to change only within the range of about 27 to 31 inches (changes between 686 to 787 millimeters) of mercury.

Using a glass column filled with mercury and inverting it in a pool of mercury Torricelli made the first barometer to measure atmospheric pressure. What units are used to measure pressure? How many torr of pressure is equal to 1.55 atm? (Conversion factor: 1 atm = 760 torr)

Pressure of gases is measured in **torr** and **atm**. Torr is the units of pressure obtained using a Torricellian Barometer shown below. Normally the Height of column is 760 mm Hg. Which is equal to 760 torr Atmospheric Pressure is 760 torr.   Other unit related to atmospheric pressure is atm.

$$1 \text{ atm} = 760 \text{ torr.}$$

Problem: Convert: a) 10.0 torr to atm. B) 61.0 cm Hg to atm c) 2.75 mm Hg to atm.
Answer:

a. $10.0 \text{ torr} \times \dfrac{1 \text{ atm}}{760 \text{ torr}} = 1.32 \times 10^{-2} \text{ atm}$

b. $61.0 \text{ cm Hg} \times \dfrac{10 \text{ mm Hg}}{1 \text{ cm Hg}} \times \dfrac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.803 \text{ atm}$

c. $2.75 \text{ mm Hg} \times \dfrac{1 \text{ atm}}{760 \text{ mm Hg}} = 0.362 \text{ atm}$

Temperature (T): Gaseous state exists normally at higher temperatures compared to liquid and solid states. Unit of temperature is Kelvin (**K**).

Amount (n): Since gases have a mass and a volume, they are considered as matter. The amount of a gas is measured in **moles**.

Gas laws equations summarizing patterns in observations as an equation between two or more variables: **Boyle's**, **Charles's**, **Avogadro's and The Ideal Gas** laws as described in section 7.4.

7.4 Boyle's Law: A Pressure-Volume Relationship

In the mid 1600's, **Robert Boyle** studied the relationship between the pressure **p** and the volume **V** of a confined gas held at a constant temperature. Boyle observed that the product of the pressure and volume are observed to be nearly constant. The product of pressure and volume is exactly a constant for an **ideal gas**. Volume of a gas is **inversely proportional** to its pressure.

Mathematically put: $V \propto 1/P$, $V = k \ 1/P$

$$V_i/V_f = P_f/P_i \qquad \text{or} \qquad P_1V_1 = P_2V_2$$

Problem: If a gas has initial pressure 1.0, final volume 0.30 L of volume, and 0.50 atm of final pressure what is its initial volume?

Answer:

$$V_i/V_f = P_f/P_i$$

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

$$V_i = \frac{(0.50 \text{ atm})(0.30 \text{ L})}{1.0 \text{ atm}} = 0.15 \text{ L}$$

7.5 Charles's Law: A Temperature-Volume Relationship

At constant n and P, the volume of a gas increases proportionately as its absolute temperature (K) increases. If the absolute temperature is doubled, the volume is doubled. Volume is **directly proportional** to temperature in **Kelvin**.

Mathematically put**:** $\qquad$ **V α T;** $\qquad$ **V = kT** $\qquad\qquad$ $V_1/T_1 = V_2/T_2$

Problem: If 3.00 L of gas at 25°C is heated to 564 K what would be the final volume of the gas?

Answer:
Initial temperature: 25°C + 273 = 298 K;
Final temperature = 546 K; initial volume = 3.00 L.

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

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

$$V_f = \frac{(3.00 \text{ L})(546 \text{ K})}{298 \text{ K}} = 5.50 \text{ L}$$

7.6 The Combined Gas Law Combined Gas Law

Boyles and Charles Laws were combined to an equation:

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

$$P_i V_i T_f = P_f V_f T_i$$

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

Problem: P_i = 1.00 atm P_f = 0.800 atm
          V_i = 2.30 L V_f = ? L
          T_i = 25°C T_f = 20°C

Answer:

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

and substituting:

$$V_f = \frac{(1.00 \text{ atm})(2.50 \text{ L})(20°C + 273)}{(0.800 \text{ atm})(25°C + 273)}$$

$$V_f = \frac{(1.00 \text{ atm})(2.50 \text{ L})(293 \text{ K})}{(0.800 \text{ atm})(289 \text{ K})} = 3.07 \text{ L}$$

Avogadro's Law

Volume of a gas is **directly** proportional to moles of gas at constant T and P.

Mathematically put: **V α n;   V = kn; $V_1/n_1 = V_2/n_2$**

                         n = moles of gas

Problem: A gas sample at certain pressure contains 0.25 moles of H_2 and has 1.00 L of volume. More H_2 gas were added while maintaining the same pressure and final volume increased to 3.00 L. How many moles of H_2 were added?

Answer: Begin by assuming that V_i is 1.0 L. Consequently, V_f must be 3.0 L.

$$\frac{V_i}{n_i} = \frac{V_f}{n_f}$$

$$n_f = \frac{V_f n_i}{V_i}$$

$$n_f = \frac{(3.0 \text{ L})(0.25 \text{ mol } H_2)}{1.0 \text{ L}} = 0.75 \text{ mol } H_2$$

7.7 The Ideal Gas Law

An ideal gas can be characterized by three <u>state variables</u>: absolute pressure (P), volume (V), and absolute temperature (T).

$$PV=nRT$$

n = number of <u>moles</u>
R = Uiversal gas constant = **0.08206** L atm/mol = **62.4** L torr/mol K
Problem: What would be the pressure (in atm) of 4.80 g of H_2 at 25 C if it has a volume of 20.0 L?

 Answer: $\qquad\qquad\qquad$ PV = nRT

Solving for pressure, P, $\qquad$ $P = \dfrac{nRT}{V}$

$$P = \frac{nRT}{V}$$

$$n = 4.80\,g\,H_2 \times \frac{(1\,mol\,H_2)}{2.02\,g\,H_2} = 2.38\,mol\,H_2$$

$$R = \frac{0.0821\,L \cdot atm}{K \cdot mol}$$

T = 25°C + 273 = 298 K; V = 20.0 L
Substituting,

$$P = \frac{(2.38\,mol\,H_2)(0.0821\,L \cdot atm/K \cdot mol)(298\,K)}{20.0\,L} = 2.91\,atm$$

Ideal Gas Concept
An **ideal gas** is defined to be a system in which there are no intermolecular/interatomic forces (hydrogen bonding, dipole-dipole attraction, Londodn dispersion forces). Such a system can only exist as a gas. Any real system will approach ideal gas behavior in the limit that the pressure is extremely low and the temperature is high enough to overcome attractive intermolecular forces.

7.8 Dalton's Law of Partial Pressures

John Dalton studied the effect of gases in a mixture. He observed that the **Total Pressure** of a gas mixture was the sum of the Partial Pressure of each gas.

$$P_{total} = P_1 + P_2 + P_3 + \ldots\ldots P_n$$

Partial Pressure is defined as the pressure of a single gas in the mixture as if that gas alone occupied the container. In other words, Dalton maintained that since there was an enormous amount of space between the gas molecules within the mixture that the gas molecules did not have any influence on the motion of other gas molecules, therefore the pressure of a gas sample would be the same whether it was the only gas in the container or if it were among other gases.

A gas corresponding to these assumptions is called an **ideal gas**; as the temperature of a real gas is lowered, or its pressure is raised, its behavior no longer resembles that of an ideal gas because one or more of the assumptions of the theory is no longer valid.

Problem: A gaseous mixture containing helium (He) and neon (Ne), has 0.56 atm of total pressure. If the partial pressure of He is 0.27 atm, what would be the partial pressure of Ne?

Answer:

$$P_{total} = P_{He} + P_{Ne}$$
$$P_{Ne} = P_t - P_{He}$$
$$P_{Ne} = 0.56 \text{ atm} - 0.27 \text{ atm}$$
$$P_{Ne} = 0.29 \text{ atm}$$

Chemistry at a Glance: The Gas Laws
7.9 Changes of State

As the temperature of a gas is decreased, the molecules can be condensed to liquids and then to solids. Slowly moving molecules are attracted to each other easily and results in **changes of gaseous state** to more **condensed phases**: liquid and solids. Ionic compounds never exist as gases since very high temperature is required in overcoming strong electrostatic attraction between the ions. The physical state of a compound is determined by the temperature and the kinetic energy as well as the intermolecular forces in the substance.

The Liquid State

When considering the three states of matter, the middle state is known as the Liquid State. It has some of the characteristics of the solid state and some of the characteristics of the gas state.

- Like the gas state, the liquid state tends to flow, or have fluidity.
- Like the gas state, the liquid state tends to take on the shape of the container that it is in.
- Like the solid state, the liquid state is associated with somewhat low kinetic energy.

Compressibility
Unlike the gaseous state liquid state has cannot be compressed. Like the solid state, the liquid state tends to have very little ability to be compressed. The fact break fluid in a vehicle works with no air leaks into break line is based on non compressibility of liquids.
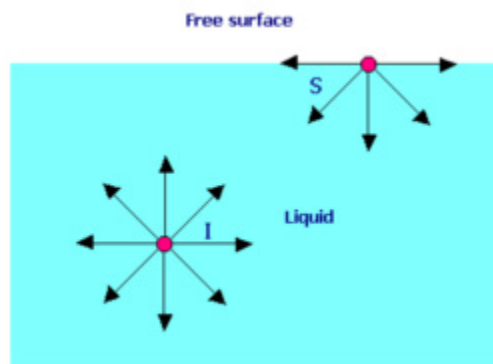
Viscosity
Viscosity is a measure of a fluid's resistance to flow. Liquids such as molasses or motor oil are examples of highly viscous substances. The viscosity of a liquid generally decreases as

the temperature is increased. Gases also have a resistance to flow, although these viscosities are much lower than for liquids.

Surface Tension

A molecule I in the interior of a liquid is under attractive forces in all directions and the vector sum of these forces is zero. But a molecule S at the surface of a liquid is acted by a net inward cohesive force that is perpendicular to the surface. Surface tension is the tendency of the surface of a liquid to behave like a stretched elastic membrane. There is a natural tendency for liquids to minimize their surface area. For this reason, drops of liquid tend to take a spherical shape in order to minimize surface area. For such a small droplet, surface tension will cause an increase of internal pressure p in order to balance the surface force.

A molecule I in the interior of a liquid is under attractive forces in

Surface tension of a liquid leads to following:

Cohesive forces: Intermolecular forces between molecules on the surface of a substance.

Adhesive forces: Intermolecular forces between two different types of molecules at the Interface between two substances.

Capillary action: Rising of a liquid through a capillary due to the overwhelming adhesive forces over the cohesive forces.

7.10 Evaporation of Liquids
7.11 Vapor Pressure of Liquids

One of the most fundamental qualities of a liquid is the vapor pressure that the liquid produces. Vapor is the term that is used to describe the gas phase material that is located directly above the liquid phase. By knowing the vapor pressure of a liquid, many qualities of that liquid are implied.

Vapor pressure is the pressure that is exerted by gas phase units that are leaving the surface of a liquid. The vapor pressure depends on the types of intermolecular forces present in the liquid.

1) Hydrogen Bonding (Highest vapor pressure)

2) Dipole-dipole Forces
3) London Dispersion (Van der Waals) Forces (Lowest vapor pressure)

7.12 Boiling and Boiling Point

The boiling point of an element or a substance is the temperature at which the vapor pressure of the liquid equals the environmental pressure surrounding the liquid. A liquid in a vacuum environment has a lower boiling point than when the liquid is at atmospheric pressure. A liquid in a high pressure environment has a higher boiling point than when the liquid is at atmospheric pressure. In other words, the boiling point of liquids varies with and depends upon the surrounding pressure. At higher elevations liquids boils at lower temperature and food need to be cooked longer. In a pressure cooker it need to cooked less since the boiling temperature has increased significantly.

The boiling point is also significantly affected by the factors that affect the vapor pressure and depends on the types of intermolecular forces present in the liquid.

1) Hydrogen Bonding (Lowest vapor pressure and boils at higher temperature).
2) Dipole-dipole Forces
3) London Dispersion (Highest vapor pressure and boils at lower temperature).

The Solid State

The solid state is the most highly ordered state of matter; the strong attractive forces between particles impart a definite shape to the solid. Solids are incompressible. Solids may be **crystalline** (regular, repeating structure) or **amorphous** (without organized structure).

The crystalline solids

Crystalline solids are based upon a simple pattern of arrangement of molecules that is repeated many times throughout the molecule often there will be boundaries in the material where the pattern cannot be continued, these give rise to the edges of crystals and a polycrystalline material. The crystalline solids may be classified into three major groups:

1) **Covalent solids** or **molecular solids**: Low melting, nonconductive solids
2) **Ionic solids:** High melting, nonconductive and brittle solids.
3) **Metallic solids**. High melting, malleable, and conducting solids.
Ionic compounds never exist as gases since very high temperature is required in overcoming strong electrostatic attraction between the ions.

7.13 Intermolecular Forces in Liquids and Solids

Intermolecular forces are the attractions that exist among particles or atoms/molecules of matter in any of the two phases of matter liquids and solids, found on earth. The strength of these forces increases as the matter change its phase from liquid to a solid. Ideal gases have no intermolecular forces compare to liquids and solids and solids

have the strongest forces. Ionic solids and metallic solids donot have molecules and therefore their antiparticle attractions are stronger and treated separately from intermolecular forces.

1) Ionic solids: The inter-ion forces in ionic solids are so strong that they exist only as solids even at very higher temperatures. Ionic solids have ionic interactions, the strong electrostatic attractions between oppositely charged ions to form a ionic lattice (the ionic bond) as in sodium chloride, NaCl(s).

2) Metallic solids: The inter atomic forces between metals atoms is metallic solid created by **metallic bond** sharing electrons between many metal atoms are so strong they exist only as solids even at higher temperatures. Ionic solids have ionic interactions, the strong electrostatic attractions between oppositely charged ions to form a ionic lattice (the ionic bond) as in sodium chloride, NaCl(s).

3) Covalent Liquid and Solids:

 Other forms of weaker intermolecular forces resulting from polar covalent bonds in molecules (hydrogen bonding and dipole-dipole forces) and the polarization of electrons on non-polar covalent molecules (London dispersion forces). These weaker intermolecular forces are classified according to their strength as shown below:

Intermolecular forces: Intermolecular forces are three types of attractions that exist among the molecules of a covalent compound in the liquid and solid state. These are found in small molecules such as water and in giant molecules such as proteins.

i) Hydrogen bonding: Hydrogen bonding is the attraction strong dipoles present only in polar molecules that contain F-H, O-H and N-H polar covalent bond. Hydrogen bonding is a very strong attraction because elements F, O and N have the **largest electronegativities** among other elements in the periodic table. Hydrogen bonding (between O-H and O-H dipoles) in water allows water to exist as a liquid at room temperature. N-H dipole in proteins allows the formation of doubles helix structure in DNA and other complex structures found in living cells.

ii) Dipole-Dipole forces: This include the attraction between all polar molecules through the dipoles (except F-H, O-H and N-H dipoles) dipolar covalent bond formed by unequal sharing of electrons of bonds in a molecule. A molecule can be nonpolar even though it may have polar covalent bond because of the symmetry of the molecular structure canceling the bond polarities. Therefore, there are no dipole-dipole interactions in non-polar molecules.

iii) London Dispersion Forces: These forces are the weakest of all intermolecular attractions and occur in **non-polar molecules** with nonpolar covalent bonds.

What causes London dispersion forces?

The London dispersion forces results from instantaneous shifts of electron cloud of nonpolar molecules. These shifts in electron cloud create **instantaneous dipoles** with very short lifetime. A weaker attractive force results because of the short lived dipole attractions between two molecules. Non-polar molecules such as H_2 and N_2 can be cooled to liquids at very low temperature due to the existence of London Dispersion forces.

Why some nonpolar covalent molecules tend to become solids as the molecular weight increases: chlorine-Cl_2 (gas) (MW = 71), bromine-Br_2 (liquid) (MW = 160), and iodine-I_2 (solid) (MW= 254).

As the molecular weight of increases the number of electrons also increases in series of similar substances (halogen and hydrocarbons) increasing their ability to create stronger **instantaneous dipoles**. This leads to stronger London Dispersion forces tend to increase making these substances to exist as solids. Even though London dispersion forces exist in ionic solids and polar covalent compounds, their effect is masked by stronger ionic interactions and dipole-dipole interaction.

Chemistry at a Glance: Intermolecular Forces
Chemical Connections: The Importance of Gas Densities; Blood Pressure and the Sodium Ion/Potassium Ion Ratio; Hydrogen Bonding and the Density of Water