

Undergraduate Semester II

MJC-2(T): Physical Chemistry: States of Matter and Ionic Equilibrium

1. Gaseous State:

The Kinetic Molecular Theory of Ideal Gases

The gas laws that we have seen to this point, as well as the ideal gas equation, are empirical, that is, they have been derived from experimental observations. The mathematical forms of these laws closely describe the macroscopic behavior of most gases at pressures less than about 1 or 2 atm. Although the gas laws describe relationships that have been verified by many experiments, they do not tell us why gases follow these relationships.

The kinetic molecular theory (KMT) is a simple microscopic model that effectively explains the gas laws we have described. This theory is based on the following five postulates described here. (Note: The term “molecule” will be used to refer to the individual chemical species that compose the gas, although some gases are composed of atomic species, for example, the noble gases.)

Postulates of the Kinetic Molecular Theory

- Gases are composed of molecules that are in continuous motion, travelling in straight lines and changing direction only when they collide with other molecules or with the walls of a container.
- The molecules composing the gas are negligibly small compared to the distances between them.
- The pressure exerted by a gas in a container results from collisions between the gas molecules and the container walls.
- Gas molecules exert no attractive or repulsive forces on each other or the container walls; therefore, their collisions are elastic (do not involve a loss of energy).
- The average kinetic energy of the gas molecules is proportional to the kelvin temperature of the gas.

The test of the KMT and its postulates is its ability to explain and describe the behavior of a gas. The various gas laws can be derived from the assumptions of the KMT, which have led chemists to believe that the assumptions of the theory accurately represent the properties of gas molecules. We will first look at the individual gas laws (Boyle's, Charles's, Amontons's, Avogadro's, and Dalton's laws) conceptually to see how the KMT explains them. Then, we

will more carefully consider the relationships between molecular masses, speeds, and kinetic energies with temperature.

The Kinetic Molecular Theory Explains the Behavior of Gases

According to the KMT, gas pressure is exerted by rapidly moving gas molecules colliding with the walls of their container. Because of this, two things determine the pressure of a gas: 1) the number of molecules hitting a unit area of the wall per unit of time, and 2) the kinetic energy of the collisions - in other words, "how hard" the molecules are hitting the wall. This simple idea conceptually explains the behavior of gases as described by the gas laws:

- **Amontons's law:** If the temperature is increased, the average speed and kinetic energy of the gas molecules increase. If the volume is held constant, the increased speed of the gas molecules results in more frequent and more forceful collisions with the walls of the container, therefore increasing the pressure (Figure 1 (a)).
- **Charles's law:** If the temperature of a gas is increased, a constant pressure may be maintained only if the volume occupied by the gas increases. This will result in greater average distances traveled by the molecules to reach the container walls, as well as increased wall surface area. These conditions will decrease both the frequency of molecule-wall collisions and the number of collisions per unit area, the combined effects of which balance the effect of increased collision forces due to the greater kinetic energy at the higher temperature.
- **Boyle's law:** If the gas volume is decreased, the container wall area decreases and the molecule-wall collision frequency increases, both of which increase the pressure exerted by the gas (Figure 1 (b)).
- **Avogadro's law:** At constant pressure and temperature, the frequency and force of molecule-wall collisions are constant. Under such conditions, increasing the number of gaseous molecules will require a proportional increase in the container volume in order to yield a decrease in the number of collisions per unit area to compensate for the increased frequency of collisions (Figure 1 (c)).

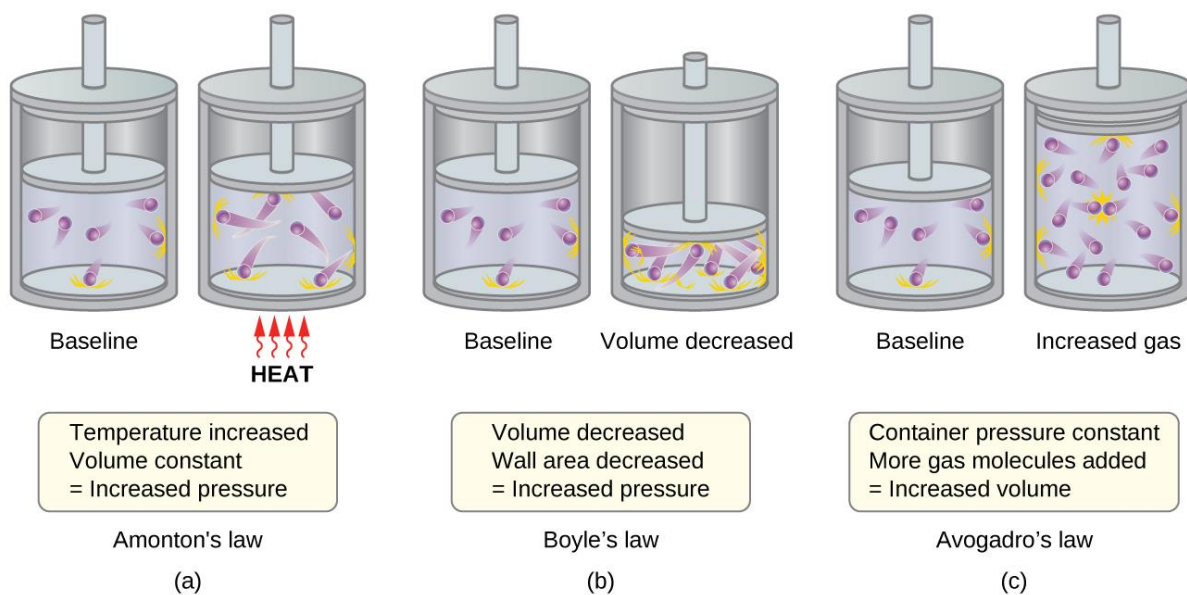


Figure 1: (a) When gas temperature increases, gas pressure increases due to increased force and frequency of molecular collisions. (b) When volume decreases, gas pressure increases due to increased frequency of molecular collisions. (c) When the amount of gas increases at a constant pressure, volume increases to yield a constant number of collisions per unit wall area per unit time.