CHAPTER FIVE

GASES

For Review

1. See Fig. 5.2 for an illustration of a barometer. A barometer initially starts with a full column of mercury which is tipped upside down and placed in a dish of mercury. The mercury in the column drops some, then levels off. The height of the column of mercury is a measure of the atmospheric pressure. Here, there are two opposite processes occurring. The weight of the mercury in the column is producing a force downward; this results in mercury wanting to flow out of the column. However, there is an opposing force keeping mercury in the column. The opposing force is that of the atmospheric gas particles colliding with the surface of the mercury in the dish; this results in mercury being pushed up into the column. When the two opposing processes are equal in strength to each other, the level of mercury in the column stays constant. The height of mercury in the column supported by the atmosphere is then a measure of pressure of the atmosphere.

See Fig. 5.3 for an illustration of a simple manometer. A manometer also has two opposing forces going against each other. There is the force exerted by the gas molecules in the flask. The opposing force is on the other side of the mercury filled U tube; it is the force exerted by atmospheric gases. The difference in height of the mercury in the U tube is a measure of the difference in pressure between the gas in the flask and the atmosphere. By measuring the height difference of mercury, one can determine how much greater than or less than the gas pressure in the flask is to the atmospheric pressure.

2. Boyle’s law: \( P \) is inversely proportional to \( V \) at constant \( n \) and \( T \). Mathematically, \( PV = k = \text{constant} \). The plot to make to show a linear relationship is \( V \) vs. \( 1/P \). The resulting linear plot has positive slope equal to the value of \( k \), and the y-intercept is the origin.

Charles’s law: \( V \) is directly proportional to \( T \) at constant \( P \) and \( n \). Mathematically: \( V = bT \) where \( b = \text{constant} \). The plot to make to show a linear relationship is \( V \) vs. \( T \). The slope of the line is equal to \( b \), and the y-intercept is the origin if the temperature is in Kelvin.

Avogadro’s law: \( V \) is directly proportional to \( n \) at constant \( P \) and \( T \). Mathematically: \( V = an \) where \( a = \text{constant} \). A plot of \( V \) vs. \( n \) gives a line with a positive slope equal to the a constant value, and the y-intercept is the origin.

3. Boyle’s law: \( T \) and \( n \) are constant. \( PV = nRT = \text{constant} \), \( PV = \text{constant} \)

Charles’s law: \( P \) and \( n \) are constant. \( PV = nRT \), \( V = \left( \frac{nR}{P} \right) T = (\text{constant}) T \)

Avogadro’s law: \( V \) and \( T \) are constant. \( PV = nRT \), \( V = \left( \frac{RT}{P} \right) n = (\text{constant}) n \)

\( P \) and \( n \) relationship at constant \( V \) and \( T \): \( PV = nRT \), \( P = \left( \frac{RT}{V} \right) n = (\text{constant}) n \)
P is directly proportional to n at constant V and T.

\[ P \propto n \text{ at constant } V \text{ and } T. \]

\[ PV = nRT, \quad P = \left( \frac{nR}{V} \right) T = (\text{constant}) T \]

P is directly proportional to T at constant V and n.

4. a. Heating the can will increase the pressure of the gas inside the can, \( P \propto T \) when V and n are constant. As the pressure increases, it may be enough to rupture the can.

b. As you draw a vacuum in your mouth, atmospheric pressure pushing on the surface of the liquid forces the liquid up the straw.

c. The external atmospheric pressure pushes on the can. Since there is no opposing pressure from the air inside, the can collapses.

d. How "hard" the tennis ball is depends on the difference between the pressure of the air inside the tennis ball and atmospheric pressure. A "sea level" ball will be much "harder" at high altitude since the external pressure is lower at high altitude. A “high altitude” ball will be "soft" at sea level.

5. Rigid container (constant volume): As reactants are converted to products, the moles of gas particles present decrease by one-half. As n decreases, the pressure will decrease (by one-half). Density is the mass per unit volume. Mass is conserved in a chemical reaction, so the density of the gas will not change since mass and volume do not change.

Flexible container (constant pressure): Pressure is constant since the container changes volume in order to keep a constant pressure. As the moles of gas particles decrease by a factor of 2, the volume of the container will decrease (by one-half). We have the same mass of gas in a smaller volume, so the gas density will increase (is doubled).

6. Boyle's law: \( P \propto \frac{1}{V} \) at constant n and T

In the kinetic molecular theory (KMT), P is proportional to the collision frequency which is proportional to \( \frac{1}{V} \). As the volume increases there will be fewer collisions per unit area with the walls of the container and pressure will decrease (Boyle's law).

Charles's law: \( V \propto T \) at constant n and P

When a gas is heated to a higher temperature, the velocities of the gas molecules increase and thus hit the walls of the container more often and with more force. In order to keep the pressure constant, the volume of the container must increase (this increases surface area which decreases the number of collisions per unit area which decreases the pressure). Therefore, volume and temperature are directly related at constant n and P (Charles’s law).

Avogadro’s law: \( V \propto n \) at constant P and T
As gas is added to a container (n increases), there will be an immediate increase in the number of gas particle collisions with the walls of the container. This results in an increase in pressure in the container. However, the container is such that it wants to keep the pressure constant. In order to keep pressure constant, the volume of the container increases in order to reduce the collision frequency which reduces the pressure. V is directly related to n at constant P and T.

Dalton’s law of partial pressure: \( P_{\text{tot}} = P_1 + P_2 + P_3 + \ldots \)

The KMT assumes that gas particles are volumeless and that they exert no interparticle forces on each other. Gas molecules all behave the same way. Therefore, a mixture of gases behaves as one big gas sample. You can concentrate on the partial pressures of the individual components of the mixture or you can collectively group all of the gases together to determine the total pressure. One mole of an ideal gas behaves the same whether it is a pure gas or a mixture of gases.

P vs. n relationship at constant V and T. From question 3, this is a direct relationship. As gas is added to a container, there will be an increase in the collision frequency, resulting in an increase in pressure. P and n are directly related at constant V and T.

P vs. T relationship at constant V and n. From question 3, this is a direct relationship. As the temperature of the gas sample increases, the gas molecules move with a faster average velocity. This increases the gas collision frequency as well as increases the force of each gas particle collision. Both of these result in an increase in pressure. Pressure and temperature are directly related at constant V and n.

7. a. At constant temperature, the average kinetic energy of the He gas sample will equal the average kinetic energy of the Cl\(_2\) gas sample. In order for the average kinetic energies to be the same, the smaller He atoms must move at a faster average velocity as compared to Cl\(_2\). Therefore, plot A, with the slower average velocity, would be for the Cl\(_2\) sample, and plot B would be for the He sample. Note the average velocity in each plot is a little past the top of the peak.

b. As temperature increases, the average velocity of a gas will increase. Plot A would be for O\(_2\)(g) at 273 K and plot B, with the faster average velocity, would be for O\(_2\)(g) at 1273 K. Because a gas behaves more ideally at higher temperatures, O\(_2\)(g) at 1273 K would behave most ideally.

8. Method 1: molar mass = \( \frac{dRT}{P} \)

Determine the density of a gas at a measurable temperature and pressure, then use the above equation to determine the molar mass.

Method 2: \( \frac{\text{effusion rate for gas } 1}{\text{effusion rate for gas } 2} = \frac{(\text{molar mass})_2}{\sqrt{(\text{molar mass})_1}} \)
Determine the effusion rate of the unknown gas relative to some known gas; then use Graham’s law of effusion (the above equation) to determine the molar mass.

9. The pressure measured for real gases is too low as compared to ideal gases. This is due to the attractions gas particles do have for each other; these attractions “hold” them back from hitting the container walls as forcefully. To make up for this slight decrease in pressure for real gases, a factor is added to the measured pressure. The measured volume is too large. A fraction of the space of the container volume is taken up by the volume of gas of the molecules themselves. Therefore, the actual volume available to real gas molecules is slightly less than the container volume. A term is subtracted from the container volume to correct for the volume taken up by real gas molecules.

10. The kinetic molecular theory assumes that gas particles do not exert forces on each other and that gas particles are volumeless. Real gas particles do exert attractive forces for each other, and real gas particles do have volumes. A gas behaves most ideally at low pressures and high temperatures. The effect of attractive forces is minimized at high temperatures since the gas particles are moving very rapidly. At low pressure, the container volume is relatively large (P and V are inversely related) so the volume of the container taken up by the gas particles is negligible.