

Physical Properties of Gases

In this chapter we will see how the state of gas can describe and how its properties depends upon its condition.

Ideal Gases:

Pressure-Volume Relation:

Boyle performed series of experiments to determine the effects of the force on the column of mercury on the volume of sample of air.

Refer to Figure 1.1 and 1.2

It was found that length of the mercury column increases and the length of the air (volume of the sample of air) column decreases.

Another experiment using a simple syringe device showed that as we increase the pressure, the corresponding volume decreases as shown above.

Also, the straight-line or linear expression is observed between P_{added} and $1/v$ results.

Refer to Figure 1.3

Force = Mass \times Gravity

$$f = mg$$

$$1 \text{ N} = 1 \text{ kg ms}^{-2}.$$

$$g \text{ on earth} = 9.81 \text{ ms}^{-2}.$$

The downward force divided by cross-sectional area gives us a pressure. The units for pressure is called as Pascal, symbol Pa.

$$1 \text{ Pa} = 1 \text{ N m}^{-2}.$$

$$1 \text{ bar} = 10^5 \text{ Pa} = 10^5 \text{ N m}^{-2}.$$

Thus, a relationship between volume of a gas and its pressure can be written as

$$P \quad 1/V \quad \text{-----} \quad (1)$$

$$PV = \text{Constant}$$

$$V \quad 1/P \quad \text{-----} \quad (1)$$

Which is know as Boyle's Law

Thus Boyle's Law can be defined as:

The volume of a sample of a gas varies inversely as the pressure, if the temperature remains constant.

According to Boyle's Law, the pressure and the volume of a sample of gas at fixed temperature vary so that the product of pressure (P) and volume (V) remains constant.

$$P_1 V_1 = P_2 V_2$$

The processes, which occur at constant temperature, are said to be isothermal. Thus the pressure-volume data often plotted as P versus V as shown in below is called as PV isotherm.

Refer to Figure 1.5

Pressure Units

Most commonly used unit is **bar** instead of atmosphere which is abbreviated as **atm**.

$$1 \text{ atm} = 1.01325 \text{ bar}$$

$$1 \text{ bar} = 75 \text{ cm of Hg}$$

$$1 \text{ atm} = 76 \text{ cm of Hg}$$

Problem 1.

What volume will a gas that behaves ideally occupy at a pressure of 0.032 bar if its volume is 3.00L at 12.0 bar and the temperature is held constant?

$$P_1 V_1 = P_2 V_2$$

$$P_1 = 0.032 \text{ bar}, P_2 = 12.0 \text{ bar}, V_1 = 12.0 \text{ L}$$

$$V_2 = \frac{P_1 V_1}{P_2}$$

$$= \frac{0.032 \text{ bar} \times 3.00 \text{ L}}{12.0 \text{ bar}}$$

$$= 1100 \text{ L}$$

Temperature-Volume Relation:

Early work by French Scientist Jacques Charles and J. L. Gay-Lussac, lead to the idea that if pressure is kept constant, the volume of the gas sample increases linearly with the temperature.

This is known as Gay-Lussac's and Charles Law:

We all know that, all gases expand when heated and contract when they are cooled. Also, for many gases the volume of the sample of the gas, at fixed, low pressure, is greater at the temperature of the normal boiling water than it is at freezing point of water. The ratio of the volumes measured at these two conditions is found to be equal to 1.366 for variety of gases.

Thus,

$$\begin{aligned} V_{bp} / V_{fp} &= 1.366 \\ V_{bp} - V_{fp} &= 0.366 V_{fp} \end{aligned}$$

Refer to Figure 1.6

From Similar Triangle,

$$\frac{0.366 V_{fp}}{100} = \frac{V_{fp}}{X}$$

$$X = 273$$

Thus, the new scale established here has unit called as Kelvin, symbol K, known as absolute temperature scale.

So we can write a equation describing the relation between the Celsius scale and Kelvin scale as;

$$^{\circ}\text{C} = \text{K} - 273$$

the more precise relation is

$$^{\circ}\text{C} = \text{K} - 273.15$$

Thus, the volume of a sample of gas, at fixed pressure, is proportional to the absolute temperature.

$$\begin{aligned} V &\propto T \text{ (at constant P)} \\ V &= (\text{const}) T \end{aligned} \quad \text{----- (2)}$$

$V/T = \text{const.}$

Problem 2

A gas sample of constant composition has a volume of 1.00 L at the sea-level conditions of 1 bar and 15°C. What is its volume in the thermosphere at 500 km, where the pressure is 1.6×10^{-11} bar and the temperature is 1580 K.

From Boyle's and Charles's Law

$PV/T = \text{constant}$

$$P_1 V_1 / T_1 = P_2 V_2 / T_2$$

$$\frac{1 \text{ bar} \times 1.00 \text{ L}}{288.15 \text{ K}} = \frac{1.6 \times 10^{-11} \text{ bar} \times V_2}{1580 \text{ K}}$$

$$V_2 = 3.4 \times 10^{11} \text{ L}$$

$PV = nRT$

The dependence of the volume of a sample of a gas on pressure and on the temperature is shown in following fig., which shows the Boyle's law hyperbolic curve at constant temperature as well as linear temperature-volume relation at constant pressure.

Refer to Figure 1.7

Thus, from equation (1) and (2) we can write:

$$V \propto T/P \quad \text{----- (3)}$$

The Mole Unit: The most convenient way of expressing sample of gas is by indicating how many numbers of molecules are present in the sample. The mole unit expresses this number.

Thus, the mole unit is defined as equal to the number of atoms in a 0.012 kg, or 12 g, sample of carbon-12. The name of the unit is mole, and abbreviated as mol.

The number of atoms in 12 g of carbon-12 is also known as Avogadro's Number. The value of Avogadro's number is 6.022×10^{23} .

Based on this number we introduce a constant, called as Avogadro's Constant, N_A , which is nothing but a Avogadro's number per mole.

$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}.$$

Now, with the symbol n for the amount of, or the number, of molecules in the gas sample, and from the equation (3), we can write:

$$V \propto n T / P$$

$$V = (\text{constant}) n T / P \quad \text{----- (4)}$$

Avogadro's Hypothesis:

Amadeo Avogadro in 1812 expressed a hypothesis, which states that samples of different gases, which contain the same number of molecules of any complexity, size, or shape, occupy the same volume at the same temperature and pressure.

Using this hypothesis, we can now introduce a same proportionality constant for all gases.

Thus, we introduce the symbol R , called gas constant.

From equation 4, we can write:

$$V = R n T / P$$

Or

$$PV = nRT \quad \text{----- (5)}$$

We generally deal with 1 mole of sample of gas.

$$P V = RT, \quad \text{where } V = V/n, \text{ which is molar volume.}$$

Thus, this expression is a summary of the empirical pressure-volume law of Boyle, the proportionality of temperature and volume and Avogadro's Hypothesis.

Gas Constant, R :

The value for Gas Constant R can be obtained from the result that at 25°C and 1 bar the volume of 1 mol of gas, which behaves ideally, is 24.789 L.

$$PV = nRT$$

$$R = PV / nT$$

$$= (24.789 \text{ L} \times 1 \text{ bar}) / (298.15 \text{ K} \times 1 \text{ mol})$$

$$= 0.083143 \text{ L bar K}^{-1} \text{ mol}^{-1}.$$

Molecular Mass from gas Density:

With m for the mass of the sample and M for the mass of 1 mol of gas molecules, the number of moles n of gas can be expressed as

$$n = m/M$$

From equation (5)

$$PV = (m/M) RT$$

$$PM = (m/V) RT$$

$$PM = d RT \quad \text{----- where } d \text{ is density given by } d = m/V$$

$$M = (d RT) / P \quad \text{----- (6)}$$

Which gives mass of 1 mol of molecules of gas in terms of density at any pressure and temperature.

Problem 3.

The cold, 10°C, pumped-up bicycle tire contained 1.00 L of air confined by a total pressure of 9.3 bar. How many moles of the molecules of air are there in the tire?

Start with an idea that 1 mol of any gas has volume 24.8 L at 25°C and 1 bar.

Let us first calculate the volume at 25°C and 1 bar.

From Boyle's and Charles's Law

$$PV/T = \text{constant}$$

$$P_1 V_1 / T_1 = P_2 V_2 / T_2$$

$$\frac{1 \text{ bar} \times V_1}{298 \text{ K}} = \frac{9.3 \text{ bar} \times 1.00 \text{ L}}{283 \text{ K}}$$

$$V_1 = \frac{1.00 \text{ L} \times 9.3 \text{ bar} \times 298 \text{ K}}{1.00 \text{ bar} \times 283 \text{ K}}$$

$$V_1 = 9.8 \text{ L}$$

Now, the number moles of the molecules can be found by

$$n = 9.8 \text{ L} / 24.8 \text{ L mol}^{-1} = 0.40 \text{ mol}$$

Gas Mixtures:

Mixtures of gases are conveniently described in terms of the partial pressures and the mole fractions of their components.

Partial Pressures:

If the pressure P needed to confine the gas mixture is found to be equal to the sum of individual partial pressures P_1, P_2, P_3, \dots needed to confine each component by itself, the gas mixture is said to obey Dalton's Law of Partial Pressure.

Thus, we can write this Law as

$$P = P_1 + P_2 + P_3 + \dots = P_j \quad \text{----- (7)}$$

Let n_1, n_2, n_3, \dots be the amounts of the molecules of the various component and let n be the total amounts of the molecules of the mixtures.

Then we can write

$$n = n_1 + n_2 + n_3 + \dots \quad \text{----- (8)}$$

The ideal-gas expression can be written for the mixture and for each component.

$$n = PV/RT, \quad n_1 = P_1V/RT, \quad n_2 = P_2V/RT \quad \dots\dots\dots$$

From equation (8)

$$PV/RT = P_1V/RT + P_2V/RT + \dots\dots\dots$$

Or

$$P = P_1 + P_2 + P_3 + \dots \quad \text{----- (9)}$$

Thus, gas mixtures obey Dalton's Law of partial pressure.

Number Fractions:

If n_j is the amount of molecules of the j th component in a particular sample and n is the total amount of molecules, the fractions of the j th component can be written as

$$x_j = n_j / n \quad \text{----- (10)}$$

This is called as mole fraction, and is equal to the ratio of the number of molecules of the jth component to the total number of molecules.

Let us divide equation (8) by n, we get

$$1 = n_1/n + n_2/n + n_3/n + \dots$$

Thus,

$$1 = x_1 + x_2 + x_3 + \dots \quad \text{----- (11)}$$

In a similar way we can define pressure fraction P_j / P .

$$P_j / P = (n_j RT / V) / (n RT / V) = n_j / n = x_j \quad \text{----- (12)}$$

Mass of 1 mol of gas Mixture is given by

$$M = x_1 M_1 + x_2 M_2 + x_3 M_3 + \dots \quad \text{----- (13)}$$

Problem 4

In a dry air at a total pressure of 1 bar, what approximate mass is calculated for 1 mol of air on the basis of the three major components with the partial pressures nitrogen, 0.78 bar; oxygen 0.21 bar; and argon, 0.01 bar?

From Equation (12)

mole fraction = pressure fraction

Thus, 1mol sample of air, there are 0.78 mol of Nitrogen, 0.21 mol of Oxygen and 0.01 mol of Argon.

Thus Mass of 1 mol of air is

$$\begin{aligned} M &= 0.78 \text{ mol} (28.0 \text{ g mol}^{-1}) + 0.21 \text{ mol} (32.0 \text{ g mol}^{-1}) + 0.01 \text{ mol} (39.9 \text{ g mol}^{-1}) \\ &= 29 \text{ g} \end{aligned}$$