

## Chapter 5 - Ideal Gases

### Learning Objectives for Today

- Become familiar with the ideal gas equation of state (Ideal gas law)
- Learn to use the ideal gas law with mixtures of ideal gases

*The next two chapters of the text deal with behaviour of gases. We start by looking at the idealized behaviour of simple gases, which can be described in terms of a very simple equation of state. Later we will look at the behaviour of real gases, which requires more complex equations. Let us start this discussion by considering what is an ideal gas.*

**Ideal Gas:** An ideal gas is a gas whose pressure, volume and temperature can be related by the following equation of state:

$$PV = nRT, \quad (5.18)$$

or

$P(V/n) = RT$ , which can be written as

$$Pv = RT$$

Where:

$P$  = Pressure of the gas (Pa)

$V$  = Total volume of the gas ( $\text{m}^3$ )

$n$  = Number of moles of the gas present in the volume  $V$ , (number)

$R$  = Universal gas constant ( $\text{J/mol.K}$ )

$T$  = Absolute temperature (K)

$v$  = molar volume (Volume of one mole of the gas)

Equation 5.18 is called the ideal gas equation of state or ideal gas law. Any gas whose behaviour can be described by this equation of state would be called an ideal gas.

*Let us also define what is meant by "equation of state."*

**Equation of state:** Any equation that describes the relationship between two or more intensive properties of a substance is called an equation of state.

The ideal gas equation is a relationship between three intensive variables:  $P$ ,  $T$ , ( $V/n = v_m$ ). Note that although the total volume,  $V$ , is not an intensive variable,  $V/n$  (which is same as the molar volume) is an intensive variable.

Simple gases like nitrogen, hydrogen, oxygen etc. at normal temperatures and pressures obey the ideal gas law.

*The ideal gas law was not discovered by one person. It took several people and a time span of more than a century to discover this simple law. Subsets of this law were discovered independently and are associated with the names of their inventors.*

**Boyle's Law** is a the ideal gas law applied to constant temperature systems

$$PV = \text{Constant at constant } T$$

or

$$P_1V_1 = P_2V_2 = P_3V_3 \dots\dots\dots (T = \text{Const.})$$

If the product of pressure and volume was measured at a different temperature, the value would of course be different. So one could write the Boyle's law as

$$PV = f(T)$$

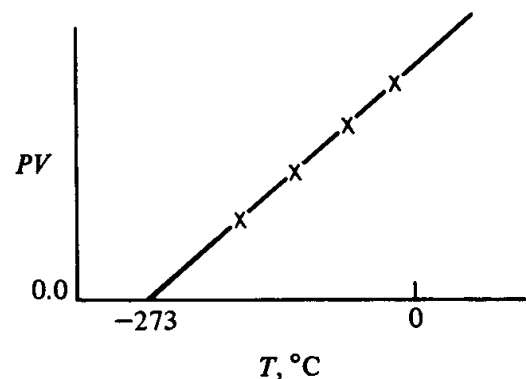
Note: The notation  $f(T)$  stands for "a function of temperature."

**Charles' law.** He measured the product  $PV$  of a gas at different temperatures and plotted the numbers against temperature. He saw the following picture.

The equation of the straight line can be written as

$$PV = m [T (\text{in } ^\circ\text{C}) + 273],$$

Where, 'm' is the slope of the straight line. It was later found that a more accurate value of the intercept was 273.15 and this intercept actually defined a new temperature scale.



You already knew that this temperature scale is the absolute temperature scale. Now you also know how it originated. In terms of the absolute temperature, the equation could be written as

$$PV = mT$$

The slope  $m$  was later found to be related to the number of moles of present in the system, which made the equation identical to the ideal gas law.

$$PV = nRT.$$

### 5.2.1 Universal Gas Constant

All gases approach ideal gas law behaviour at low pressures, i.e.

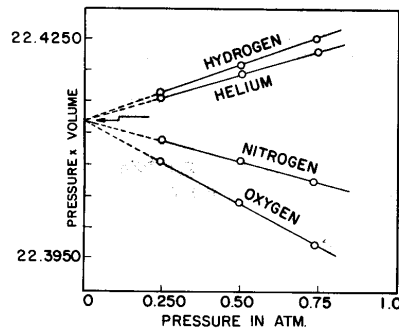


Figure 5-3 Evaluation of Ideal Gas Pressure-Volume Product at 0°C for One Kilomole

22.414 m<sup>3</sup>.atm.

$$\lim_{P \rightarrow 0} \left[ \frac{PV}{nT} \right] = R \quad \text{for all gases.}$$

Data have been collected for a variety of gases as shown in Fig. 5.3. It shows that at a constant temperature, the product PV for one kmol of all gases, when extrapolated to zero pressure converges to same value. At 0 °C, this value is

It is found that at 0° C (273.15K) and 101.325 kPa (1 atm) 1 kmol of an ideal gas will occupy 22.414 m<sup>3</sup> of volume. Therefore,

$$\begin{aligned} R &= \frac{101.325 \times 10^3 \times 22.414}{1 \times 273.15} \frac{(\text{Pa})(\text{m}^3)}{(\text{kmol})(\text{K})} \\ &= 8.314 \times 10^3 \frac{(\text{Pa})(\text{m}^3)}{(\text{kmol})(\text{K})} \\ &= 8314 \frac{\text{J}}{\text{kmol K}} \end{aligned}$$

### 5.3 Ideal Gas Mixture

The basic concept to remember is that a mixture containing several ideal gases will also behave like an ideal gas with

$n = n_1 + n_2 + n_3 + \dots + n_c$ , where  $n$  is the total number of moles of the mixed gas and  $n_i$  is the number of moles of the  $i^{\text{th}}$  component.

There are special laws which were discovered independently but are all related to this simple concept.

#### Dalton's Law

At a fixed temperature and constant volume, the pressure of a mixture of ideal gases is equal to the sum of pressures which would be exerted by each of the gases individually in the same volume.

To illustrate this: At a constant temperature, take N number of identical gas bottles. Fill each with a different gas to some pressure, i.e. bottle 1 to  $P_1$ , bottle 2 to  $P_2$  etc.

Now transfer all of these gases to one bottle of the same volume. According to Dalton's law the pressure in this bottle would be

$$P = P_1 + P_2 + P_3 + \dots + P_N$$

The Dalton's law is a natural outcome of the ideal gas law if one assumes that different ideal gases can be added together to obtain a mixed gas which will also behave ideally.

Let us say you have N different ideal gases and their numbers of moles in the mixture are:

$$\text{Gas-1} = n_1; \text{Gas-2} = n_2; \text{gas-3} = n_3 \text{ etc.}$$

When these gases are mixed together the total number of moles would be  $(n_1 + n_2 + n_3 + \dots + n_N)$ .

If the volume is fixed at V and the temperature is kept constant at T, the pressure of the mixed gas is given by

$$\begin{aligned} P &= nRT/V = (n_1 + n_2 + n_3 + \dots + n_N)RT/V \\ &= n_1RT/V + n_2RT/V + n_3RT/V + \dots + n_NRT/V \\ &= P_1 + P_2 + P_3 + \dots + P_N \end{aligned}$$

It means that in a volume containing a mixture of ideal gases the partial pressures of individual components can be added to get the mixture pressure. Partial pressures are denoted by a bar on top of the letter P. In this notation,

$P = \bar{P}_1 + \bar{P}_2 + \bar{P}_3 + \dots + \bar{P}_N$ , where P = total pressure and  $\bar{P}_i$  is the partial pressure of  $i^{\text{th}}$  component. We have already seen that the total pressure can be written as,

$$\begin{aligned} P &= n_1RT/V + n_2RT/V + n_3RT/V + \dots + n_NRT/V \\ &= (n_1/n)(nRT/V) + (n_2/n)(nRT/V) + (n_3/n)(nRT/V) + \dots + (n_N/n)(nRT/V) \end{aligned}$$

where  $n = (n_1 + n_2 + n_3 + \dots + n_N)$ , or the total number of moles in the mixture. From ideal gas law we can see that

$nRT/V = P$ . We can also see that  $n_1/n$  is the mole fraction of gas 1,  $n_2/n$  is the mole fraction of gas 2 in the mixture and so on.

Therefore the above equation can be written as

$$P = y_1P + y_2P + y_3P + \dots + y_NP$$

The terms on the right hand side represent the contribution of each component toward the total pressure. In other words, these terms are the partial pressures of individual components. Therefore, we can say

$$\bar{P}_i = y_iP, \text{ where } y_i \text{ is the mole fraction of the } i^{\text{th}} \text{ component.}$$

It says that the partial pressure of an individual component in a gas mixture is equal to its mole fraction multiplied by the total pressure.

### AMAGAT'S LAW.

So far we considered the situation in which temperature and volume were kept constant and the pressures were added. The same type of analysis can be applied to the situation in which pressure and temperature are kept constant and volumes are added together.

The volume of a mixture of ideal gases is given by

$$\begin{aligned} V &= \frac{nRT}{P} \\ &= \frac{(n_1 + n_2 + n_3 + \dots + n_N)RT}{P} \\ &= \frac{n_1RT}{P} + \frac{n_2RT}{P} + \frac{n_3RT}{P} + \dots + \frac{n_NRT}{P} \\ &= V_1 + V_2 + V_3 + \dots + V_N \end{aligned}$$

Which means that the partial volumes can be added. The statement that the partial volumes are additive is called AMAGAT'S LAW.

### Example Problem 5-1

Five cubic meters of CH<sub>4</sub> and 15 m<sup>3</sup> of CO<sub>2</sub> are held separately at 95 kPa and 30°C. The gases are then mixed and the mixture is maintained at 95 kPa and 30°C.

Determine

- the volume of the mixture,
- the mole fractions of CH<sub>4</sub> and CO<sub>2</sub> in the mixture,
- the partial pressures of CH<sub>4</sub> and CO<sub>2</sub> in the mixture,

- (d) the average molar mass of the mixture,  
 (e) the density of the mixture.

### Solution

- a) Since the initial temperature and pressure of the gases are the same as for the mixtures, Amagat's Law can be applied and the total volume of the mixture is  $(5 + 15) \text{ m}^3$  or

$$V = 20 \text{ m}^3.$$

- b) The total volume found in part (a) can be calculated from the perfect gas law, i.e.,

$$V = nRT/P$$

where,  $n$  is the number of moles of  $\text{CO}_2$  and  $\text{CH}_4$  combined. The perfect gas law can also be applied to each of the pure gases separately, giving

$$\begin{aligned} V_1 &= n_1RT/P \text{ and} \\ V_2 &= n_2RT/P \end{aligned}$$

for  $\text{CH}_4$  and  $\text{CO}_2$ , respectively.

Since  $T$  and  $P$  have the same values for the pure gases and for the gas mixture, the ratio of volumes gives

$$V_1/V = n_1/n = Y_1 \text{ and}$$

$$V_2/V = n_2/n = Y_2.$$

That is, the ratio of partial volume to total volume is the mole fraction.

Therefore,

$$Y_2 = V_2/V = 15/20 = 0.75.$$

This is the mole fraction of carbon dioxide. The mole fraction of methane is:

$$Y_1 = 1 - 0.75 = 0.25.$$

- (c) The partial pressures are evaluated from Equation 5.22:

$$P_1 = 0.25(95) \text{ or } 23.75 \text{ kPa}$$

$$P_2 = 71.25 \text{ kPa}$$

- (d) The total number of moles is determined from the ideal gas equation of state (Equation 5.18):

$$PV = nRT$$

Where, T is (30 + 273.15) or 303.15 K, V is 20 m<sup>3</sup>, P is 95 x 10<sup>3</sup> Pa and R is 8.314 J/mol K. Therefore,

$$n = \frac{95 \times 10^3 \times 20}{8.314 \times 303.15} = 753.85 \text{ moles}$$

The number of moles of methane is  $y_1 n$  or 188.46 moles. The rest is carbon dioxide. The molar masses of CH<sub>4</sub> and CO<sub>2</sub> are 16.04 and 44.01 kg/kmol respectively. Therefore, the total mass of the mixture is

$$\frac{(188.46)(16.04)}{1000} + \frac{(565.39)(44.01)}{1000}$$

or 27.905 kg. The average molar mass for the mixture is hence

$$\frac{27.905}{0.754} = 37.02 \frac{\text{kg}}{\text{kmol}}$$

The average molar mass of a gas mixture can in general be found more simply from

$$M = \sum y_i M_i$$

In this case,

$$M = (0.25)(16.04) + (0.75)(44.01) = 37.02 \text{ kg/kmol}$$

(e) The density of the mixture is

$$27.905 \text{ kg} / 20 \text{ m}^3 = 1.395 \text{ kg/m}^3$$

***Note: All of the material up to the end of section 5.3 boils down to two basic principles.***

- 1. The ideal gas law, i.e.  $PV = nRT$***
- 2. The statement that a mixture of ideal gases also behaves like an ideal gas with the total number of moles being equal to the sum of moles of individual components.***