

UNIT – 1

Properties of Gases and Mixtures

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Important Repeated Questions:

1. **Explain/Define Vander Waal's Equation of State. Derive an expression for Evaluation of Constant 'a' and 'b'.**
(S25 - Q2c, 07 marks) (S23 - Q2c, 07 marks) (W22 - Q2 OR, 07 marks) (W23 - Q1c, 07 marks)
2. **Define/State and explain Avogadro's law.**
(W24 - Q1a) (W23 - Q1a, 03 marks)
3. **What is compressibility chart? What are the observations can be made from this chart?**
(S25 - Q5 OR a, 03 marks) (S24 - Q1a)

Legends: W- Winter, S- Summer, Q- Question and 03/04/07- Marks of Question

1.1 Introduction

- ▶ Up to this point, we have limited our consideration to thermodynamic systems that involve a single pure substance.
- ▶ Many important thermodynamic applications, involve mixtures of several pure substances rather than a single pure substance. It is important to develop an understanding of mixtures and learn how to handle them.
- ▶ In this unit, we deal with *non-reacting gas mixtures* treated as a pure substance (homogeneous mixture of different gases (E.g. air).
- ▶ The properties of a gas mixture depend on the properties of the individual gases (called components or constituents) as well as on the amount of each gas in the mixture.

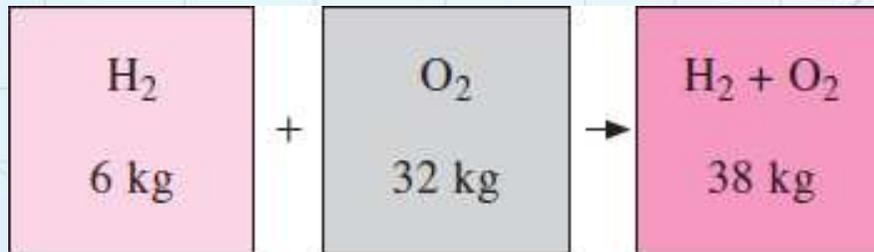


Fig.1.1 – Mixtures of gases

- ▶ It is not practical to prepare property tables for every conceivable mixture composition, since the number of possible compositions is endless.
- ▶ Therefore, we need to develop rules for determining mixture properties from a knowledge of mixture composition and the properties of the individual components. We do this first for ideal-gas mixtures and then for real-gas mixtures.

1.2 Avogadro's Law

- ▶ *Avogadro's law* is an experimental gas law relating the volume of a gas to the amount of substance of gas present. The law is a specific case of the ideal gas law.
- ▶ “*Avogadro's law* states that the number of moles of any gas is proportional to the volume of the gas at a given pressure and temperature.”

OR

- ▶ “Under the same condition of temperature and pressure, equal volumes of all gases contain the same number of molecules.”
- ▶ Mathematically, the law can be written as,

$$V \propto n \text{ and } \frac{V}{n} = k$$

Where,

‘*V*’ is volume of gaseous mixture at temperature *T*,

‘*n*’ is the amount of substance of the gas (measured in moles),

‘*k*’ is a constant for a given temperature and pressure.

1.3 Equation Of State For An Ideal Gas

- ▶ Property tables provide very accurate information about the properties, but they are bulky and vulnerable to typographical errors.
- ▶ A more practical and desirable approach would be to have some simple relations among the properties that are sufficiently general and accurate.
- ▶ “Any equation that relates the independent properties, such as pressure, temperature, and specific volume of a substance is called an *equation of state*.”
- ▶ A perfect gas obeys Boyle’s law and Charle’s law. These two laws may be combined to formulate equation of state to determine the relationship between pressure, volume and temperature.
- ▶ Consider m kg mass of perfect gas undergoing a change from state 1 to state 2 by two processes: 1-A at constant pressure and A-2 at a constant temperature as shown in Fig.1.2. Process 1-A obeys Charle’s law and process A-2 obeys Boyle’s law.
- ▶ **Process 1-A:** by applying Charle’s law,

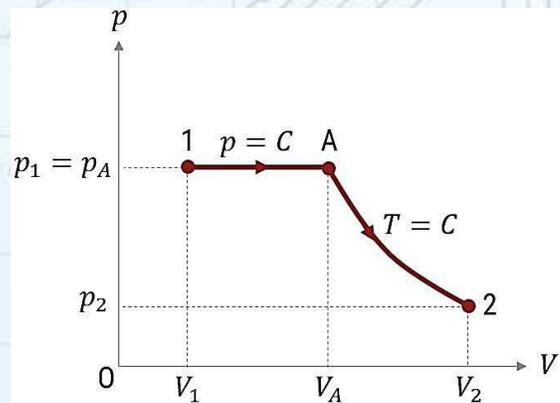


Fig.1.2 – p - V diagram for combined gas law

$$\begin{aligned} \frac{V_1}{T_1} &= \frac{V_A}{T_A} \\ \therefore \frac{V_1}{T_1} &= \frac{V_A}{T_2} \quad (\because T_A = T_2) \\ \therefore V_A &= V_1 \times \frac{T_2}{T_1} \end{aligned} \quad \text{Eq. (1.1)}$$

- ▶ **Process A–2:** by applying Boyle’s law,

$$\begin{aligned} p_A V_A &= p_2 V_2 \\ \therefore p_1 V_A &= p_2 V_2 \quad (\because p_A = p_1) \\ \therefore V_A &= V_2 \times \frac{p_2}{p_1} \end{aligned} \quad \text{Eq. (1.2)}$$

- ▶ By, comparing eq. (1.1) and (1.2) we get,

$$\begin{aligned} V_1 \times \frac{T_2}{T_1} &= V_2 \times \frac{p_2}{p_1} \\ \therefore \frac{p_1 V_1}{T_1} &= \frac{p_2 V_2}{T_2} \\ \therefore \frac{pV}{T} &= \text{Constant} \end{aligned} \quad \text{Eq. (1.3)}$$

- ▶ The magnitude of the constant depends on the type of gas and it is known as **Characteristic Gas Constant (R)**. For m kg of gas,

$$\begin{aligned} \frac{pV}{T} &= mR \\ \therefore pV &= mRT \end{aligned} \quad \text{Eq. (1.4)}$$

This equation is known as equation of state for an ideal gas.

- ▶ For unit mass of kg the above equation can be rewritten as,

$$\therefore pv = RT \quad \text{Eq. (1.5)}$$

Where, p = absolute pressure, N/m²

v = specific volume, m³/kg

T = absolute temperature, K and

- ▶ For engineering calculations, the equation of state for ideal gases can be used for real gases so long as the pressures are well below their critical pressure and the temperatures are above the critical temperature.
- ▶ At a *very low pressure and at a very high temperature*, real gases like hydrogen, oxygen, nitrogen, helium etc. behave nearly the same way as ideal gases.

1.4 Vander Waal's Equation For Real Gas

The ideal-gas equation of state is very simple, but its range of applicability is limited. It is desirable to have equations of state that represent the p, v, T behavior of substances accurately over a larger region with no limitations.

Such equations are naturally more complicated. Several equations have been proposed for this purpose but we shall discuss only Van der Waal's equation.

1.4.1 Real Gas

- ▶ It has been observed that when experiments are performed at relatively low pressures and temperatures most of the real gases obey Boyle's and Charles's laws quite closely.
- ▶ But the actual behaviour of real gases at elevated pressures and at low temperatures deviates considerably. The ideal gas equation $pv = RT$ can be derived analytically using the kinetic theory of gases by making the following assumptions :
 - i. A finite volume of gas contains large number of molecules.
 - ii. The collision of molecules with one another and with the walls of the container are perfectly elastic.
 - iii. The molecules are separated by large distances compared to their own dimensions.
 - iv. The molecules do not exert forces on one another except when they collide.
- ▶ As long as the above assumptions are valid the behaviour of a real gas approaches closely that of an ideal gas.

1.4.2 Expression For Vander Waal's Equation

- ▶ The van der Waal's equation of state was proposed with **two constants** that are determined from the behavior of a substance at the critical point.
- ▶ Van der Waal's intended to improve the ideal-gas equation of state by including **two correction factors** not considered in the ideal-gas equation. These two corrective effects are: (a) the intermolecular attraction forces and (b) the volume occupied by the molecules themselves.
- ▶ The term a/v^2 accounts for the intermolecular forces, and '**b**' accounts for the volume occupied by the gas molecules. These two correction factors are discussed in detail as below:

Correction factor 'a' for an intermolecular attraction forces:

- ▶ Let consider the *forces of cohesion* which act between a molecule and those surrounding it. When the molecule is sufficiently far removed from the surface of the gas in all directions the resultant of these cohesive forces are equally probable, as the individual forces are varying continuously as the surrounding molecules change their positions.
- ▶ Hence if the resultant is averaged over a sufficient length of time the aggregate force will be nil. This is not true, however, when the molecule is near the surface.
- ▶ Let the force from each molecule be resolved into normal and tangential components. All directions for the resultant in the tangential plane are equally likely, but the resultant normal component is most often directed inwards. Averaged over a sufficient length of time the total resultant force will therefore be a normal force always directed inwards.
- ▶ Thus the average effect of the cohesive forces is the same as if there was a permanent field of force acting at and near the surface. This field of force can be regarded as exerting a pressure p_1 over the boundary of the gas.
- ▶ The pressure is proportional to the number of molecules per unit area near the boundary surface and to the normal component of the force. Both of these factors are proportional to the density, so p_1 will be proportional to the square of the density.

$$p_1 = a\rho^2 \quad \text{Eq. (1.6)}$$

where, 'a' is constant, by replacing ρ^2 by $\frac{a}{v^2}$ we can write,

$$p_1 = \frac{a}{v^2} \quad \text{Eq. (1.7)}$$

- ▶ Hence the molecules are not deflected by impact alone on reaching the boundary, but as the total result of their impact and of the action of the supposed field of force. Their change of momentum may be supposed to be produced by a **total pressure $p + p_1$** instead of by the **simple pressure p** .
- ▶ With this correction, the ideal gas equation of state $pv = RT$ can be replaced by,

$$(p + p_1)v = RT$$
$$(p + \frac{a}{v})v = RT \quad \text{Eq. (1.8)}$$

Correction factor 'b' for the volume occupied by the molecules themselves:

- ▶ The characteristic equation for a perfect gas is obtained by neglecting the finite size of the molecules. If this be taken into account it is obvious that the equation must be modified, for the distance travelled by a molecule between two successive encounters will be less than if the molecules were point spheres.

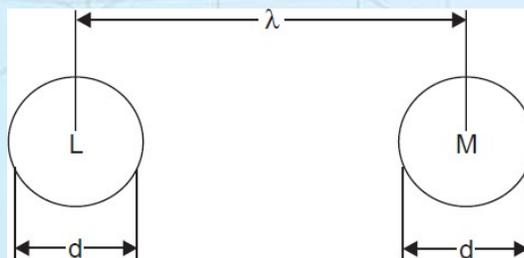


Fig.1.3 – Volume occupy by the molecules

- ▶ Let the average distance traversed by a molecule between two successive encounters be denoted by λ , the mean free path.

- ▶ In Fig. 1.3, suppose L and M to be the two molecules of diameter 'd' at a distance λ apart. If these molecules were to impinge along the line of centres the path moved over would be less by an amount 'd' than if the molecules were point spheres.
- ▶ Now all the encounters between molecules are not direct, so their mean free paths will be lessened by an amount kd , where k is a fraction. That is, the mean free path is diminished in the ratio $(\lambda - kd) : \lambda$ or $(1 - \frac{kd}{\lambda}) : 1$.
- ▶ If the mean free path is lessened in this ratio, the encounters per second will be increased in the ratio 1: $(1 - \frac{kd}{\lambda})$. But the pressure of the gas depends upon the encounters per second with the wall of the containing vessel. Hence the new pressure is given by,

$$p = \frac{1}{3} \rho C^2 \cdot \frac{1}{1 - \frac{kd}{\lambda}} \quad \text{Eq. (1.9)}$$

where ρ is the density and C is the average velocity.

- ▶ The mean free path is inversely proportional to the density of the gas, for if the volume were halved, i.e., the density doubled, there would be twice as many molecules in the same space, and therefore any molecule would only have to travel approximately half as far before encountering another molecule.
- ▶ Hence writing v for $\frac{1}{\rho}$ and b for $\frac{kd}{\lambda}$ in eq. (1.9), we get

$$pv \left(1 - \frac{b}{v}\right) = \frac{C^2}{3} = RT \quad \text{Eq. (1.10)}$$

$$p(v - b) = RT \quad \text{Eq. (1.11)}$$

- ▶ Van der Waal's proposed to correct this eq. (1.11) by replacing v with the quantity $(v - b)$, where b represents the volume occupied by the gas molecules per unit mass.
- ▶ By introducing two correction factors, the ideal gas equation of state $pv = RT$ can be replaced by p with $(p + \frac{a}{v^2})$ and v with the quantity $(v - b)$, then the Van der Waal's equation of state for real gas is given by,

$$\left(p + \frac{a}{v^2}\right) (v - b) = RT \quad \text{Eq. (1.12)}$$

1.4.3 Evaluation of Constants 'a' and 'b'

- ▶ The determination of the two constants appearing in eq. 1.12 is based on the observation that the critical isotherm on a $p - v$ diagram has a horizontal inflection point at the critical point.

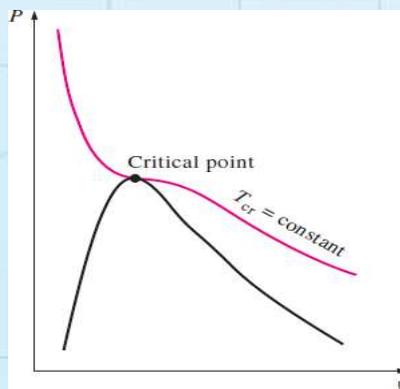


Fig.1.4 – Critical isotherm of a pure substance has an inflection point at the critical state

- ▶ Thus, the first and the second derivatives of p with respect to v at the critical point must be zero.

$$\text{That is, } \left(\frac{\partial p}{\partial v}\right)_{T=T_r=const} = 0 \text{ and } \left(\frac{\partial^2 p}{\partial v^2}\right)_{T=T_r=const} = 0$$

- ▶ Van der Waals' equation being a cubic in v has three roots which may be either all real, or two imaginary and one real, as imaginary roots always occur in pairs. There is one isothermal where there are three real coincident roots at a point of inflexion.
- ▶ All the isothermals for temperatures higher than that corresponding to the isothermal with three real coincident roots have no horizontal tangent, and all those lower have a maximum and minimum. Consequently this curve is identified with the critical isothermal. The temperature of the critical isothermal is obtained in the following manner.

$$v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{av}{p} - \frac{ab}{p} = 0 \quad \text{Eq. (1.13)}$$

- ▶ The Van der Waals equation of state for real gas is given by,

$$\begin{aligned} \left(p + \frac{a}{v^2}\right)(v - b) &= RT \\ pv - pb + \frac{a}{v^2} \times v - \frac{a}{v^2} \times b - RT &= 0 \\ pv - pb + \frac{a}{v} - \frac{ab}{v^2} - RT &= 0 \end{aligned}$$

- ▶ Multiplying both sides by $\frac{v^2}{p}$, we get

$$\begin{aligned} pv \times \frac{v^2}{p} - pb \times \frac{v^2}{p} + \frac{a}{v} \times \frac{v^2}{p} - \frac{ab}{v^2} \times \frac{v^2}{p} - RT \frac{v^2}{p} &= 0 \\ v^3 - \left(b + \frac{RT}{p}\right)v^2 + \frac{av}{p} - \frac{ab}{p} &= 0 \end{aligned} \quad \text{Eq. (1.14)}$$

The eq. (1.12) may be written as above.

- ▶ Now at the critical point, as the three roots are equal, the equation must be of the form of,

$$(v - v_c)^3 = 0 \quad \text{Eq. (1.15)}$$

where the suffix 'c' denotes conditions at the critical point. For the critical point eq. (1.14) becomes,

$$v^3 - \left(b + \frac{RT_c}{p_c}\right)v^2 + \frac{av}{p_c} - \frac{ab}{p_c} = 0 \quad \text{Eq. (1.16)}$$

Equations (1.15) and (1.16) are identical, hence equating coefficients,

$$3v_c = b + \frac{RT_c}{p_c}, \quad 3v_c^2 = \frac{a}{p_c}, \quad v_c^3 = \frac{ab}{p_c}$$

and from these by a simple reduction, we have

$$v_c = 3b, \quad p_c = \frac{a}{27b^2}, \quad T_c = \frac{8}{27} \cdot \frac{a}{bR}$$

- ▶ From these equations it follows that the critical volume, pressure, and temperature are all completely determined by the constants of equation (1.12). This equation indicates the critical constants for a particular gas and leads to the following results :
- ▶ The values of 'a' and 'b' are also given by,

$$a = 3p_c v_c^2 = \frac{9}{8} RT_c v_c = \frac{27R^2 T_c^2}{64p_c} \quad \text{Eq. (1.17)}$$

$$b = \frac{v_c}{3} = \frac{RT_c}{8p_c} \quad \text{Eq. (1.18)}$$

- ▶ The constants ‘a’ and ‘b’ are determined to be,

$$a = \frac{27R^2T_c^2}{64p_{cr}} \quad \text{and} \quad b = \frac{RT_c}{8p_{cr}} \quad \text{Eq. (1.19)}$$

- ▶ The constants ‘a’ and ‘b’ can be determined for any substance from the criticalpoint data alone.

1.5 Reduced Properties

- ▶ Gases behave differently at a given temperature and pressure, but they behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures. The normalization is done by introducing *reduced properties*.
- ▶ “The ratios of pressure, temperature and specific volume of a real gas to the corresponding critical values are called the *reduced properties*.”
- ▶ Let,

p, v, T = actual pressure, temperature and specific volume of a gas

p_c, T_c, v_c = critical pressure, temperature and specific volume of a gas

p_r, T_r, v_r = reduced pressure, temperature and specific volume of a gas

Mathematically,

$$p_r = \frac{p}{p_c}, T_r = \frac{T}{T_c}, v_r = \frac{v}{v_c} \quad \text{Eq. (1.20)}$$

1.6 Law Of Corresponding States

- ▶ The law of corresponding states state that “If any two gases have equal values of reduced pressure and reduced temperature, then they have same values of reduced volume”.
- ▶ Mathamatically, $v_r = f(T_r, p_r)$ for all gases and the function is the same.
- ▶ The compressibility factor **Z** factor for all gases is approximately the same at the same reduced pressure and temperature. (refer topic 1.7 for compressibility factor **Z**).
- ▶ The experimentally determined Z values are plotted against p_r and T_r for several gases. The gases seem to obey the principle of corresponding states reasonably well.
- ▶ This law is most accurate in the vicinity of the critical point. The *critical point* is defined as the point at which the saturated liquid and saturated vapor states are identical.

1.7 Compressibility Chart

- ▶ The ideal-gas equation is very simple and thus very convenient to use. However gases deviate from ideal-gas behavior significantly at states near the saturation region and the critical point.
- ▶ This deviation from ideal-gas behavior at a given temperature and pressure can accurately be accounted for by the introduction of a correction factor called the *compressibility factor*.
- ▶ “The compressibility factor is a correction factor to account for deviation from ideal-gas behavior at a given temperature and pressure.”

- ▶ The compressibility factor is denoted by **Z**. Mathematically,

$$Z = \frac{pv}{RT} \quad \text{Eq. (1.21)}$$

- ▶ The compressibility factor **Z** of any gas is a function of only two properties, $Z = f(T_r, p_r)$ except near the critical point.
- ▶ For ideal gas, $Z = 1$ and the value of Z for any real gas may be less or more than unity, depending on pressure and temperature conditions of the gas.
- ▶ The farther away Z is from unity, the more the gas deviates from ideal-gas behavior.
- ▶ The **general compressibility chart** is plotted with Z versus p_r for various values of T_r as shown in Fig. 1.5.

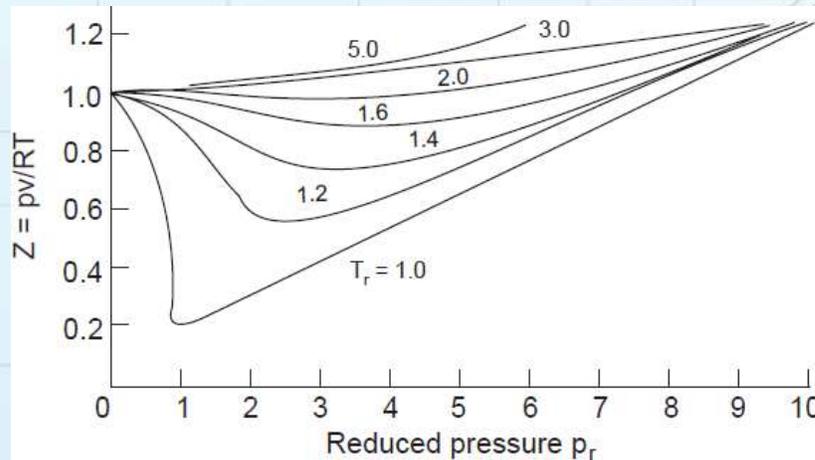


Fig.1.5 – Compressibility chart

- ▶ It is constructed by plotting the known data of one or more gases and can be used for any gas.
- ▶ This chart gives best results for the regions well removed from the critical state for all gases.

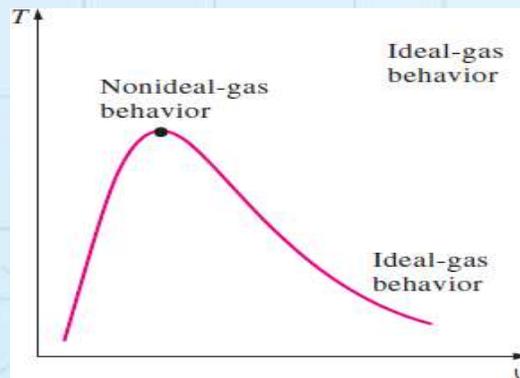


Fig.1.6 – Gases deviate from the ideal-gas behavior the most in the neighborhood of the critical point

- ▶ The following observations can be made from the generalized compressibility chart:
 1. At very low pressures ($p_r \ll 1$), gases behave as an ideal gas regardless of temperature.
 2. At high temperatures ($T_r > 2$), ideal-gas behavior can be assumed with good accuracy regardless of pressure (except when $p_r \gg 1$).
 3. The deviation of a gas from ideal-gas behavior is greatest in the vicinity of the critical point.

1.8 References

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- 3) Engineering Thermodynamics by R.K. Rajput, Laxmi Publicatins