MODULE V
IDEAL GAS AND REAL GAS MIXTURE

OBJECTIVE: **To Calculate Thermodynamics properties of real gases at all ranges of pressure, temperatures using modified equation of state including Vander Waals equation, Redlich Wong equation and Beattie-Bridgeman equation**

STRUCTURE:
5.1 Ideal gas laws:
5.2 Ideal gas equation (or) characteristic equation for the gases
5.3 Avogadro hypothesis:
5.4 Relations between properties of an ideal gas:
5.5 Relation between specific heat of gases and gas constant
5.6 Psychrometric properties
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5.8 Ideal gas mixture
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5.10 Amagats law of partial volume or additive volume:
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5.12 Expression for molecular weight (m) :
5.13 Enthalpy of gaseous mixture (h):
5.14 change in entropy of gaseous mixture (s):
5.15 Partial pressure ratio = mole fraction = volume fraction
5.16 Real gases
    5.17 Vanderwaals equation of state
    5.18 Compressibility ratio
    5.19 Compresibility chart
5.20 Critical Constants of the van der Waals Gas

IDEAL GAS

An ideal gas is an imaginary gas having no forces of intermolecular attraction so that the behavior of a molecule is not influenced by the presence of the other molecules and obeys the lay PV = RT at all pressures and temperatures. This relation Is called the ideal gas equation of state.

5.1 IDEAL GAS LAWS:

1) **BOYLE'S LAW :**The volume of a given gas is inversely proportional to the absolute pressure when temperature remains constant during the change of state"

$$V \propto 1/P \qquad\qquad PV = \text{Constant} \qquad\qquad P_1V_1 = P_2V_2 = \text{constant}$$

2) **GAY LUSSACS LAW :** The volume of a given gas is directly proportional to the absolute temperature when pressure remains constant during the change of state

$$V \propto T \qquad\qquad V/T = \text{Constant} \qquad\qquad \frac{V_1}{T_1} = \frac{V_2}{T_2} = constant$$

3) **CARLE'S LAW :** The pressure of a given gas is directly proportional to the absolute temperature when volume remains constant during the change of state

$$P \propto T \qquad\qquad P/T = \text{Constant} \qquad\qquad \frac{P_1}{T_1} = \frac{P_2}{T_2} = constant$$

5.2 Ideal gas equation (or) characteristic equation for the gases:

The relation exist between all three variables P,V,T of the gas under consideration. This relationship is called characteristic gas equation This equation can be derived by combining boyle's and charle's law.

Fig shows that a gas undergoes an arbitrary change from state 1 to state 2 and follows a path $1 - A - 2$, i.e a constant pressure process $(1 - A)$ and a constant temperature process $(A - 2)$
Applying Charles law to the process 1- A , and assuming unit mass of gas

$$\frac{V_1}{V_A} = \frac{T_1}{T_A}$$

$$V_A = \frac{T_2 \times V_1}{T_1} \quad (T_A = T_2) \dots\dots\dots (1)$$

Applying Boyle's law to the process A-2

$$\frac{V_2}{V_A} = \frac{P_1}{P_2} \quad (P_A = P_1)$$

$$V_A = \frac{P_2 \times V_2}{P_1} \dots\dots\dots\dots(2)$$

equating equation (1) and (2) we get

$$\frac{T_2 \times V_1}{T_1} = \frac{P_2 \times V_2}{P_1}$$

$$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$$

Since state 1 and 2 are arbitrarily selected, it follows that

$$\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2} = \frac{P_3 \times V_3}{T_3} = \frac{P_4 \times V_4}{T_4} = \text{constant} \ldots\ldots\ldots\ldots(3)$$

The constant is known as the **CHARACTERISTIC GAS CONSTANT**

Equation 3 can be written as

$$\frac{P \times V}{T} = R \quad \text{for unit mass}$$

$$PV = mRT \quad \text{for mass m}$$

5.3 Avagadro hypothesis:

It states that "**Equal volume of all ideal gases under identical conditions of temperature and pressure have equal number of molecules**"

that is 1 mole of any gas contains 6.022×10^{23} MOLECULES And the number is called asAVAGADRO'S NUMBER

He proved that at normal temperature and pressure (NTP) that is at $T = 0^0$ C 0R 273 K , $P = 760$ mm of Hg $= 1.013 \times 10^5$ N/m^2 the volume of 1 Kg mole ($\overline{V}$) of the gas is equal to 22.416 m^3.

The volume per mole of a substance is called MOLAR VOLUME denoted by $\overline{V}$

$$\overline{V} = \frac{V}{n}$$

where , n = number of moles $= \frac{m}{M}$

$PV = mRT$

$PV = n\, m\, R\, T$

$P\overline{V}\, n = n\, m\, R\, T$

$P\overline{V} = M\, R\, T$

The quantity " MR" is a UNIVERSAL GAS CONSTANT ($\overline{R}$)

$P\overline{V} = \overline{R}\, T$

The universal gas constant is a Physical constant whose value is given by

$$\overline{R} = \frac{P \times \overline{V}}{T} = 1.013 \times 10^5 \times \frac{22.416}{273} = 8.31773 \text{ K J / Kg mol K}$$

$\overline{R} = 8.31773$ K J / Kg mol K

5.4 Relation between properties of an ideal gas:

1) **INTERNAL ENERGY AND ENTHALPY CHANGE OF AN IDEAL GAS:**

   i) Constant volume specific heat for an ideal gas

   $$C_V = \frac{du}{dT} \quad \text{where u = internal energy}$$

ii)   **Change in internal energy** = du = C_V . dT   this equation hold good for an ideal gas for any process.

NOTE : For any other substance it is true only for the constant volume process

$$\int_1^2 du = C_V \int_1^2 dT$$
$$u_2 - u_1 = C_v\,(T_2 - T_1) \ \ldots\ldots..\ (4)$$

iii)   **constant pressure specific heat for an ideal gas**

$$C_P = \frac{dh}{dT} \ \text{where h = Enthalpy}$$

Change in enthalpy = dh = C_P . dT   this equation hold good for an ideal gas for any process.

NOTE : For any other substance it is true only for the constant pressure process

$$\int_1^2 dh = C_P \int_1^2 dT$$

$$h_2 - h_1 = C_P\,(T_2 - T_1)\ldots\ldots..(5)$$

5.5 Relation between specific heat of gases and gas constant :

h = u + pv

where, h = enthalpy

        u = internal energy

h = u + RT

in differential form

dh = du + RdT

Substituting for du and dh we get

C_p dT = $C_v$du +RdT

$C_p = C_v + R$

$R = C_p - C_v$

The ratio of specific heats C_p and C_v is again a constant and is a function of temperature only and is represented by γ (gama)

$\gamma = \frac{C_P}{C_V}$ ....(6)

$R = C_p - C_v$ ....(7)

$\frac{R}{C_V} = \frac{C_P}{C_V} - 1$ (dividing by C_V)

by rearranging we get

$$C_V = \frac{R}{\gamma - 1}$$

Similarly by dividing equ (7) by C_P we get

$$C_P = \frac{R \times \gamma}{\gamma - 1}$$

Psychrometry

Psychrometry is the study of the properties of mixtures of air and water vapour.

5.6 Psychrometric properties:

Dry-bulb temperature (DBT)

The dry-bulb temperature is the temperature indicated by a thermometer exposed to the air in a place sheltered from direct solar radiation. The term dry-bulb is customarily added to temperature to distinguish it from wet-bulb and dewpoint temperature

Wet-bulb temperature (WBT)

The thermodynamic wet-bulb temperature is a thermodynamic property of a mixture of air and water vapor. The value indicated by a wet-bulb thermometer often provides an adequate approximation of the thermodynamic wet-bulb temperature.

Dew point temperature

The saturation temperature of the moisture present in the sample of air, it can also be defined as the temperature at which the vapour changes into liquid (condensation)

Specific Humidity

Specific humidity is defined as the proportion of the mass of water vapor and mass of the moist air sample (including both dry air and the water vapor); it is closely related to humidity ratio and always lower in value.

Absolute humidity

The mass of water vapor per unit volume of air containing the water vapor. This quantity is also known as the water vapor density.

Relative humidity

The ratio of the vapor pressure of moisture in the sample to the saturation pressure at the dry bulb temperature of the sample.

Specific enthalpy

Analogous to the specific enthalpy of a pure substance. In psychrometrics, the term quantifies the total energy of both the dry air and water vapour per kilogram of dry air

Specific volume

Analogous to the specific volume of a pure substance. However, in psychrometrics, the term quantifies the total volume of both the dry air and water vapour per unit mass of dry air.

Psychrometric ratio

The psychrometric ratio is the ratio of the heat transfer coefficient to the product of mass transfer coefficient and humid heat at a wetted surface. It may be evaluated with the following equation

5.7 Psychrometric chart

A Psychrometric chart raphically represents the thermodynamic properties of moist air. Standard psychrometric charts are bounded by the dry-bulb temperature line (abscissa) and the vapour pressure or humidity ratio (ordinate). The Left Hand Side of the psychrometric chart is bounded by the saturation line. Figur shows the schematic of a psychrometric chart. Psychrometric charts are readily available for standard barometric pressure of 101.325 kPa at sea level and for normal temperatures (0-50˚C).
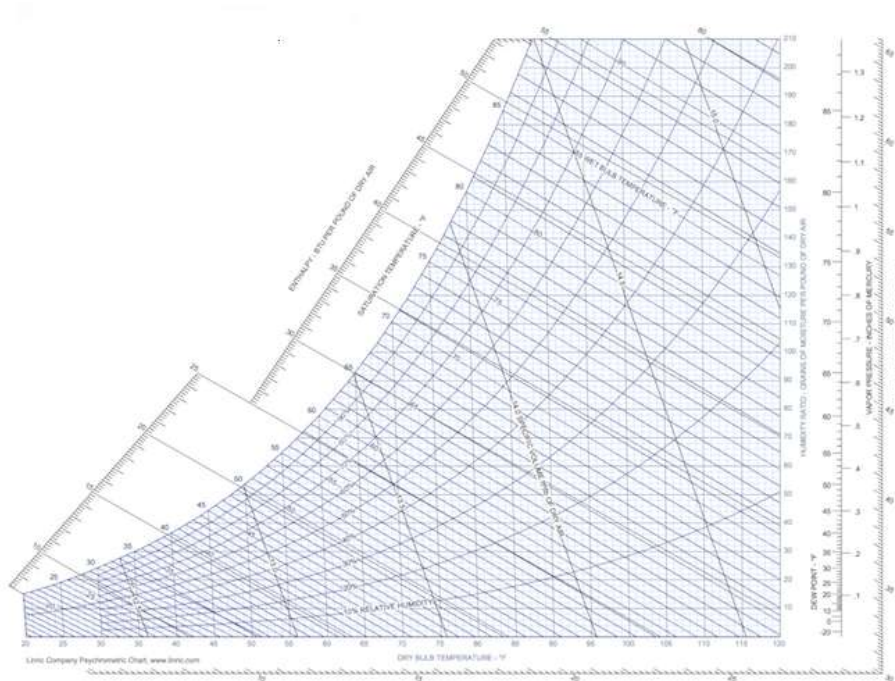
- Dry-bulb temperature (*DBT*) is that of an air sample, as determined by an ordinary thermometer. It is typically plotted as the abscissa (horizontal axis) of the graph. The SI units for temperature are kelvins or degrees Celsius; other units are degrees Fahrenheit and degrees Rankine.
- Wet-bulb temperature (*WBT*) is that of an air sample after it has passed through a constant-pressure, ideal, adiabatic saturation process, that is, after the air has passed over a large surface of liquid water in an insulated channel. In practice this is the reading of a thermometer whose sensing bulb is covered with a wet sock evaporating into a rapid stream of the sample air (see Hygrometer). When the air sample is pre-saturated with water, the WBT will read the same as the DBT. The slope of the line of constant WBT reflects the heat of vaporization of the water required to saturate the air of a given relative humidity.

- Dew point temperature (*DPT*) is the temperature at which a moist air sample at the same pressure would reach water vapor "saturation." At this point further removal of heat would result in water vapor condensing into liquid water fog or, if below freezing point, solid hoarfrost. The dew point temperature is measured easily and provides useful information, but is normally not considered an independent property of the air sample as it duplicates information available via other humidity properties and the saturation curve.
- Relative humidity (*RH*) is the ratio of the mole fraction of water vapor to the mole fraction of saturated moist air at the same temperature and pressure. RH is dimensionless, and is usually expressed as a percentage. Lines of constant RH reflect the physics of air and water: they are determined via experimental measurement. The concept that air "holds" moisture, or that moisture "dissolves" in dry air and saturates the solution at some proportion, is erroneous see relative humidity for further details.
- Humidity ratio is the proportion of mass of water vapor per unit mass of dry air at the given conditions (DBT, WBT, DPT, RH, etc.). It is also known as the moisture content or mixing ratio. It is typically plotted as the ordinate (vertical axis) of the graph. For a given DBT there will be a particular humidity ratio for which the air sample is at 100% relative humidity: the relationship reflects the physics of water and air and must be determined by measurement. The dimensionless humidity ratio is typically expressed as grams of water per kilogram of dry air, or grains of water per pound of air (7000 grains equal 1 pound).
- Specific enthalpy, symbolized by *h*, is the sum of the internal (heat) energy of the moist air in question, including the heat of the air and water vapor within. Also called heat content per unit mass. In the approximation of ideal gases, lines of constant enthalpy are parallel to lines of constant WBT. Enthalpy is given in (SI) joules per kilogram of air, or BTU per pound of dry air.

5.8 Ideal gas mixture:

Consider a mixture of perfect gases A, B C etc existing in equilibrium at pressure P and occupying a volume V , at temperature T . Each constitutes occupies the same volume that the entire mixture occupies and each constituent is at same temperature of the mixture

Constituents	Properties	Mixture
A	P_a , V , T , m_a , n_a	
B	P_b , V , T , m_b , n_b	P , V , T , m , n
C	P_c , V , T , m_c , n_c	

From the table it can be seen that (taking mass as an example) the total mass of the mixture is equal to the sum of the masses of the individual gases, $m = m_a + m_b + m_c$

- **Mass fraction (m_f) :**

    Mass fraction of the constituent gas is the ratio of the mass of the constituent gas to the total mass of the mixture of perfect gases

$$m_{fa} = \frac{m_a}{m} \ , m_{fb} = \frac{m_b}{m} \ , m_{fc} = \frac{m_c}{m}$$

$$m = m_a + m_b + m_c$$

$$\frac{m}{m} = \frac{m_a}{m} + \frac{m_b}{m} + \frac{m_c}{m}$$

$$1 = m_{fa} + m_{fb} + m_{fc}$$

- **Mole (n) :** A mole of a substance has a mass numerically equal to the weight of the substance
- **Mole fraction (X or n_f) :** The total number of moles of the mixture is equal to the sum of the moles of the individual gas

$$n = n_a + n_b + n_c$$

The mole fraction of any component is the ratio of the number of moles of the constituent gas to the total number of moles of the mixture of perfect gases

mole fraction of gas A, B and C is given by $X_a = \frac{n_a}{n}$, $X_b = \frac{n_b}{n}$, $X_c = \frac{n_c}{n}$ respectively

$$n = n_a + n_b + n_c$$
$$\frac{n}{n} = \frac{n_a}{n} + \frac{n_b}{n} + \frac{n_c}{n}$$
$$X = X_a + X_b + X_c$$

5.9 Gibbs daltons law:

The total pressure of a mixture of perfect gases is equal to the sum of the partial pressure of the constituent gases if each component exists separately at the same temperature and volume as the mixture. If this component pressure is denoted by p_i , then Daltons law can be written as

$$P = \sum_{i=1}^{j} P_i$$

Considering 3 gases A,B , C

GASES A, B, C	=	GAS A V, T, P_a , m_a , n_a	+	GAS B V, T, P_b , m_b, n_b	+	GAS C V, T, P_c , m_c , n_c
Schematic representation of Daltons law of partial pressure						

$$P = P_a + P_b + P_c$$
$$\frac{P}{P} = \frac{P_a}{P} + \frac{P_b}{P} + \frac{P_c}{P}$$
$$1 = P_{fa} + P_{fb} + P_{fc}$$

where P_f is pressure fraction

in general we can write $P_f = \sum_{i=1}^{j} P_{fi} = 1$

- ➤ **Partial pressure of a gas** (P_i) in a mixture of perfect gases is the pressure that it would exert if it alone occupied the whole volume of the mixture at same temperature.
- ➤

5.10 Amagats law of partial volume or additive volume:

It states that "Total volume (V) of a mixture of gases is equal to the sum of the volume, each component would occupy if each component exists separately at the same temperature and pressure as that of the mixture". If its component is denoted by V_i , Amagats law can be written as

$$V = \sum_{i=1}^{j} V_i$$

Considering 3 gases we can write $V = V_a + V_b + V_c$

GASES A, = B, C	GAS A P, T, V_a , m_a , n_a	+	GAS B P, T, V_b , m_b, n_b	+	GAS C P, T, V_c , m_c , n_c
Schematic representation of Amagats law of partial volume					

$$V = V_a + V_b + V_c$$
$$\frac{V}{V} = \frac{V_a}{V} + \frac{V_b}{V} + \frac{V_c}{V}$$
$$1 = V_{fa} + V_{fb} + V_{fc}$$

where V_f is volume fraction

in general we can write $\quad V_f = \sum_{i=1}^{j} V_{fi} = 1$

5.11 Expression for gas constant for mixture of perfect gas:

PV = mRT
For 3 gases A,B, C which are at same temperature and volume as the mixture we can write
$P_a V = m_a R_a T_a$
$P_b V = m_b R_b T_b$
$P_c V = m_c R_c T_c$
But from Daltons law of partial pressures
$P = P_a + P_b + P_c$
$$\frac{mRT}{V} = \frac{m_a R_a T_a}{V} + \frac{m_b R_b T_b}{V} + \frac{m_c R_c T_c}{V}$$
R $= m_{fa} . R_a + m_{fb} . R_b + m_{fc} . R_c$

5.12 Expression for molecular weight (M) :
PV = mRT
wkt $n = \frac{m}{M}$ where $\bar{R} = Universal\ gas\ constant$, M = Molecular weight
PV = nMRT

PV = n $\bar{R}$ T   where $\bar{R}$ = $Universal\ gas\ constant$ = MR

P$\bar{v}$ = $\bar{R}$ T   Where $\bar{v}$ = specific volume = $\frac{V}{n}$

Considering 3 gases A,B,C

$$R_a = \frac{\bar{R}}{M_a}, \qquad R_b = \frac{\bar{R}}{M_b}, R_c = \frac{\bar{R}}{M_c}$$

Substituting in equation R we get

R = m_{fa} . R_a + m_{fb} . R_b + m_{fc} . R_c

$$\frac{\bar{R}}{M} = m_{fa} \frac{\bar{R}}{M_a} + m_{fb} \frac{\bar{R}}{M_b} + m_{fc} \frac{\bar{R}}{M_c}$$

$$\frac{1}{M} = \frac{m_{fa}}{M_a} + \frac{m_{fb}}{M_b} + \frac{m_{fc}}{M_c}$$

$$M = \frac{1}{\frac{m_{fa}}{M_a} + \frac{m_{fb}}{M_b} + \frac{m_{fc}}{M_c}}$$

Alternate expression for molecular weight

wkt, m = n M

for 3 gases we can write

m_a = n_a . M_a , m_b = n_b . M_b , m_c = n_c . M_c

m = m_a + m_b + m_c = n_a . M_a + n_b . M_b + n_c . M_c = n.M

M = X_a M_a + X_b M_b + X_c M_c

Internal energy of gaseous mixture (U) :

Internal energy of a mixture of ideal gases is equal to the sum of the individual energies of the constituent gases at the same pressure and temperature of the mixture.

U = U_a + U_b + U_c

m.u = m_a u_a + m_b u_b + m_c u_c

where u = specific internal energy = $\frac{U}{m}$

by differentiating we get

m . du = m_a . du_a + m_b . du_b + m_c . du_c

wkt du = C_v dT

m C_v dT = m_a C_{va} dT + m_b C_{vb} dT + m_c C_{vc} dT

$$C_V = \frac{m_a}{m} C_{Va} + \frac{m_b}{m} C_{Vb} + \frac{m_c}{m} C_{Vc}$$

C_v = m_{fa} C_{va} + m_{fb} C_{vb} + m_{fc} C_{vc}

5.13 Enthalpy of gaseous mixture (h):

The enthalpy of a mixture of perfect gas is equal to sum of the enthalpies of the constituent gases

$H = H_a + H_b + H_c$

$m.h = m_a\,h_a + m_b\,h_b + m_c\,h_c$

where h = specific enthalpy $= \frac{H}{m}$

by differentiating we get

$m \cdot dh = m_a \cdot dh_a + m_b \cdot dh_b + m_c \cdot dh_c$

wkt $dh = C_p\,dT$

$m\,C_p\,dT = m_a\,C_{pa}\,dT + m_b\,C_{pb}\,dT + m_c\,C_{pc}\,dT$

$$C_p = \frac{m_a}{m}C_{Pa} + \frac{m_b}{m}C_{Pb} + \frac{m_c}{m}C_{Pc}$$

$C_P = m_{fa}\,C_{Pa} + m_{fb}\,C_{Pb} + m_{fc}\,C_{Pc}$

5.14 Change in entropy of gaseous mixture (s):

$S = S_a + S_b + S_c$

$m.s = m_a\,s_a + m_b\,s_b + m_c\,s_c$

where s = specific entropy $= \frac{S}{m}$

by differentiating we get

$m \cdot ds = m_a \cdot ds_a + m_b \cdot ds_b + m_c \cdot ds_c$

$ds = m_{fa}\,ds_a + m_{fb}\,d\,s_b + m_{fc}\,ds_c$

Change in entropy of a gas can be calculated using the equation , $ds_a = \left[C_P\,ln\frac{T_2}{T_1} - R\,ln\frac{P_2}{P_1} \right]_a$,for gas A .

Similarly for all gases we can calculate.

5.15 For mixture of perfect gases show that partial pressure ratio = mole fraction = volume fraction

$PV = mRT$

$PV = nmRT$

$PV = n\bar{R}T$ for a mixture ……..(1)

Let us consider a GAS A

$P_aV = n_a\bar{R}T$ (applying Daltons law of partial pressure , i.e at same volume and temperature) … (2)

Dividing 2 by 1 we get

$\frac{P_aV}{PV} = \frac{n_a\bar{R}T}{n\bar{R}T}$

$\frac{P_a}{P} = \frac{n_a}{n} = X_a$

Again

PV = n$\overline{R}$T for a mixture ……..(4)

PV$_a$ = n$_a$$\overline{R}$T (applying Amagats law , i.e at same pressure and temperature) … (5)

dividing 5 by 4 we get

$\frac{V_a}{V} = \frac{n_a}{n} = X_a$ ……….(6)

From equation (6) and (3)

$\frac{P_a}{P} = \frac{V_a}{V} = \frac{n_a}{n} = X_a$ Hence proved

5.16 REAL GASES:

I.   Real gases doesn't obey ideal gas equation at all pressures and temperatures

II.   Ideal gas equation is given by

- PV = m RT
- PV = n $\overline{R}$ T , $\overline{R}$ = MR
- P v = RT , where v = V/m
- P$\overline{v}$ = $\overline{R}$T , where $\overline{v}$ = V/n

III.   A gas which follows gas laws at all ranges of pressure and temperature can be considered as an ideal gas. But no such gas exists in nature.

IV.   The REAL GASES obey very closely to ideal gas or gas laws equation when the pressure is very small or temperature is very large

V.   When the pressure increases the intermolecular forces of attraction and repulsion increases, and the volume of the molecules becomes appreciable compared to the total volume of the gases. Therefore the real gases deviate considerably from the ideal gas equation.

The behaviour of real gas approaches closely to that of the ideal gas provided the following assumptions are valid:

- Any finite volume of a gas consists of a very large number of molecules
- The molecules are separated by distances larger than compared to their own dimensions and are in a state of continuous motion.
- Molecules exert no force on one another except when they collide
- Collisions of molecules with one another and with the walls of the container are perfectly elastic.
- If the conditions of temperature and pressure are such that the assumptions are not valid then the real gases starts deviating from the ideal gas.

5.17 VANDERWAALS EQUATION OF STATE:

The ideal gas law treats the molecules of a gas as point particles with perfectly elastic collisions. This works well for dilute gases in many experimental circumstances. But gas molecules are not point masses, and there are circumstances where the properties of the molecules have an

experimentally measurable effect. A modification of the ideal gas law was proposed by Johannes D. van der Waals in 1873 to take into account molecular size and molecular interaction forces. It is usually referred to as the van der Waals equation of state.

$$\left[P + a\left(\frac{n}{V}\right)^2 \right]\left(\frac{V}{n} - b\right) = RT$$

The constants a and b have positive values and are characteristic of the individual gas. The van der Waals equation of state approaches the ideal gas law PV=nRT as the values of these constants approach zero. The constant a provides a correction for the intermolecular forces. Constant b is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules.

5.18 CRITICAL CONSTANTS OF THE VAN DER WAALS GAS:

We saw in our discussion of critical phenomena that the mathematical definition of the critical point is,

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \qquad (1)$$

and

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0 . \qquad (2)$$

In other words, the critical isotherm on a p-V diagram has a point of inflection. Equations (1) and (2) constitute a set of two equation in two unknowns, V, and T. One can test to see if an approximate equation of state gives a critical point by calculating these two derivatives for the equation of state and trying to solve the pair of equations. If a solution exists (and T and V are neither zero or infinity) then we say that the equation of state has a critical point.

Let's use this test to see if a van der Waals gas has a critical point. First we have to solve the van der Waals equation of state for pressure, p,

$$p = \frac{nRT}{V-nb} - a\frac{n^2}{V^2}. \qquad (3)$$

Now we can take the derivatives in Equations 1 and 2 and set them (independently) equal to zero.

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{nRT}{(V-nb)^2} + 2a\frac{n^2}{V^3} = 0 \qquad (4)$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_T = \frac{2nRT}{(V-nb)^3} - 6a\frac{n^2}{V^4} = 0. \qquad (5)$$

In order to stress that from here on the problem is pure algebra, let's rewrite the simultaneous equations that must be solved for the two unknowns V and T (which solutions we will call V_C and T_C),

$$-\frac{nRT}{(V-nb)^2} + 2a\frac{n^2}{V^3} = 0 \qquad (6)$$

$$\frac{2nRT}{(V-nb)^3} - 6a\frac{n^2}{V^4} = 0. \qquad (7)$$

There are several ways to solve simultaneous equations. One way is to multiply Equation (6) by,

$$\frac{2}{V-nb}$$

to get

$$-\frac{2nRT}{(V-nb)^3} + 4a\frac{n^2}{V^3(V-nb)} = 0. \qquad (8)$$

Now add equations (7) and (8). Note that in this addition the terms containing T will cancel out leaving,

$$-\frac{6an^2}{V^4} + 4a\frac{n^2}{V^3(V-nb)} = 0. \qquad (9)$$

Divide Equation (9) by $2an^2$ and multiply it by V^3 (and bring the negative term to the other side of the equal sign) to get,

$$\frac{2}{(V-nb)} = \frac{3}{V},$$ (10)

which is easily solved to get

$$V = V_c = 3nb.$$ (11)

To find the critical temperature, substitute the critical volume from Equation (11) into one of the derivatives (which equals zero) say Equation (6). This gives,

$$-\frac{nRT}{(3nb - nb)^2} + 2a\frac{n^2}{(3nb)^3} = 0,$$ (12)

which "cleans up" to give,

$$\frac{RT}{4} = \frac{2a}{27b},$$ (13)

or

$$T = T_c = \frac{8a}{27bR}.$$ (14)

The critical pressure is obtained by substituting V_C and T_C into the van der Waals equations of state as solved for p in Equation (3).

$$p_C = \frac{nRT_C}{V_C - nb} - a\frac{n^2}{V_C^2}$$

$$= \frac{nR\left(\dfrac{8a}{27bR}\right)}{3nb - nb} - a\frac{n^2}{(3nb)^2}.$$ (15 a,b)

This simplifies to,

$$p_C = \frac{a}{27b^2}.$$ (16)

Our conclusion is that the van der Waals equation of state does give a critical point since the set of simultaneous equations (Equations (1) and (2)) has a unique solution.

The van der Waals equation of state is still an approximate equation of state and does not represent any real gas exactly. However, it has some of the features of a real gas and is therefore useful as the next best approximation to a real gas. We will be deriving thermodynamic relationships (equations) using the ideal gas approximation. We can rederive some of these equations using the van der Walls equation of state in order to see how these relationships are.

5.19 Compressibility factor:

The assumption of ideal gas relation implies that:

  ➢ the gas particles take up negligible volume

  ➢ the intermolecular potential energy between particles is small

  ➢ particles act independent of one another

However, real gases deviate from ideal gas behavior. This deviation at given temperature and pressure can be accurately accounted for by introduction of a correction factor called the compressibility factor Z.

$$Z = \frac{Pv}{RT} \qquad or \qquad Pv = ZRT$$

or $Z = v_{actual} / v_{ideal}$. Obviously, Z=1 for ideal gases.

Gases behave very much the same at temperatures and pressures normalized with respect to their critical temperatures and pressures.

$$P_R = \frac{P}{P_{cr}} \qquad and \qquad T_R = \frac{T}{T_{cr}}$$

Here P_R and T_R are called the reduced pressure and temperature, respectively.

By curve-fitting all the data, the general compressibility chart is obtained which can be used for all gases.
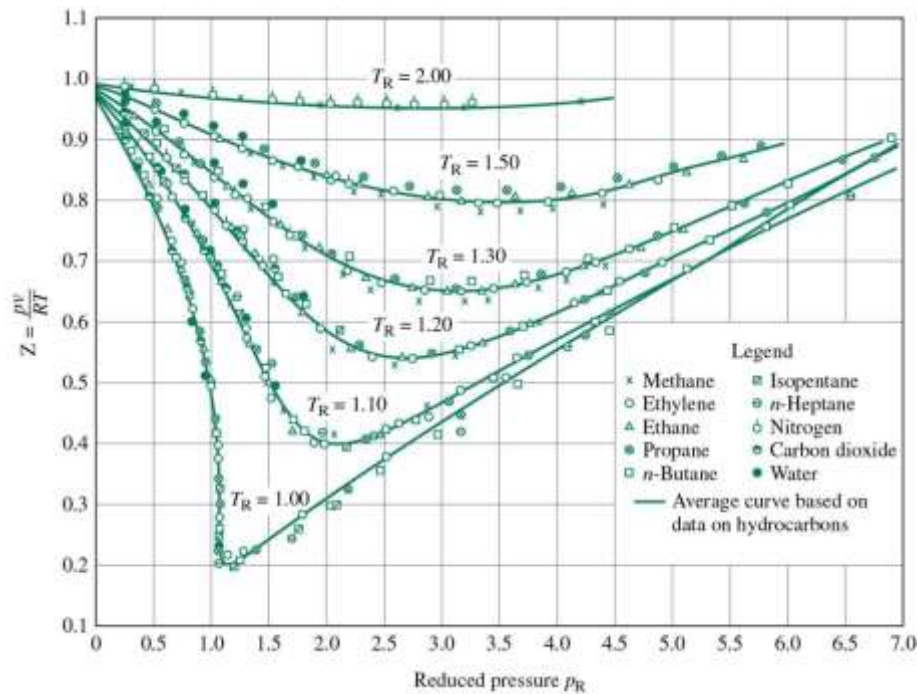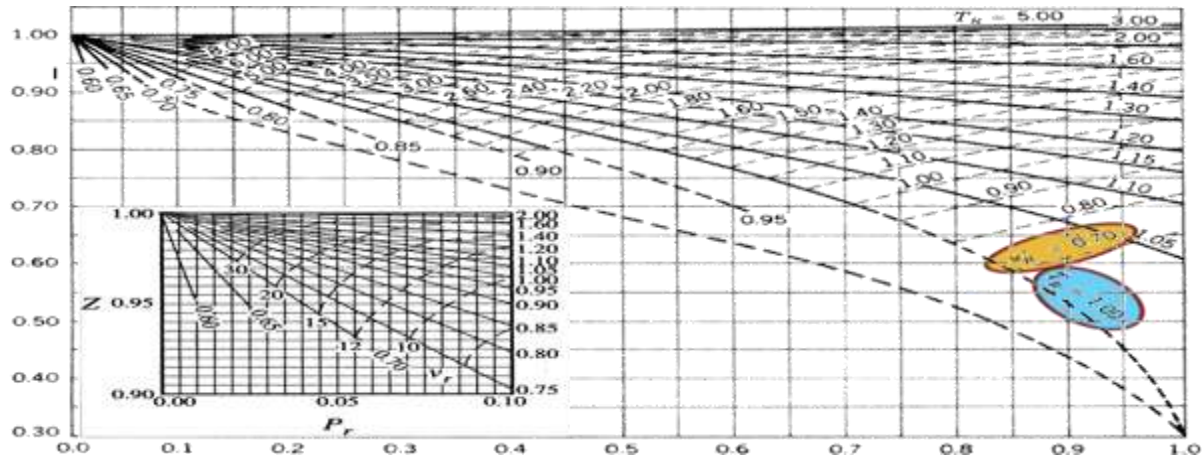

Fig. 6: Z factor, general compressibility chart.

From the Z chart, one can conclude:

➢ at very low pressure ($P_R \ll 1$), the gases behave as an ideal gas regardless of temperature

➢ at high temperatures ($T_R > 2$), ideal gas behavior can be assumed.

➢ the deviation is highest in the vicinity of the critical point.

5.20 COMPRESSIBILITY CHART:

➢ This chart is the low-pressure chart, for reduced pressures between 0 and 1 as you can see on the x-axis.
➢ Z is plotted on the y-axis.
➢ The solid curves on this diagram are the family of curves for constant reduced temperature. These curves generally run from the upper left-hand corner downwards and towards the right-hand edge of the diagram.
➢ You can tell the solid curves represent constant TR by reading the labels on the curves for TR = 1.0 and TR = 5.0 highlighted on the chart with yellow circles.
➢ The dashed curves on this diagram are the family of curves for constant ideal reduced molar volume.
➢ You can tell the dashed curves represent constant VR-ideal by reading the label on the curve for VR-ideal = 0.07, highlighted on the chart with a light blue circle.
➢ Inset on this diagram and highlighted in pale green is a very handy enlargement of the top corner of the chart, where reduced pressure is between 0 and 0.1.

The Redlich–Kwong equation is formulated as:

$$P = \frac{RT}{V_m - b} - \frac{a}{\sqrt{T}\, V_m\,(V_m + b)};$$

where:

- P is the gas pressure
- R is the gas constant,
- T is temperature,
- V_m is the molar volume (V/n),
- a is a constant that corrects for attractive potential of molecules, and
- b is a constant that corrects for volume.

> **Beattie-Bridgeman Equation of State:**

The Beattie-Bridgeman equation of state was proposed in 1928. It has five experimentally determined constants.

$$P = \frac{R_u T}{\bar{v}^2}\left(1 - \frac{c}{\bar{v}T^3}\right)(\bar{v} + B) - \frac{A}{\bar{v}^2}$$

$$A = A_0\left(1 - \frac{a}{\bar{v}}\right) \qquad B = B_0\left(1 - \frac{b}{\bar{v}}\right)$$

IMPORTANT QUESTIONS:

1. State Gibbs Daltons law of partial pressures and hence derive an expression for the gas R of a mixture of gas
2. Write a brief note on Compressibility factor and compressibility chart
3. Derive critical constants of the Van-der-Waals gas.
4. A cylinder of volume $1m^3$ is filled with a mixture of 1 Kg of CO_2 and 2 Kg of N_2 at 27 degree Celsius. Determine 1. Pressure of the mixture 2) gas constant for the mixture 4) Mole fraction of N_2 and CO_2 and 4) Molecular weight of the mixture
5. Determine the mass of nitrogen contained in a $35m^3$ vessel at 200bar and 200K by using ideal gas equation and Compressibility chart.
6. Determine the pressure exerted by CO_2 in a container of $1.5m^3$ capacity when it contains 5 Kg at 27 degree Celsius 1) using idea gas equation and 2) Van-der-Waal's equation
   Solution:
   i) Ideal gas equation PV = mRT

   $$p = \frac{m \times \overline{R} \times T}{V \times M} = \frac{5 \times 8.3143 \times 300}{1.5 \times 44}$$
   p = 188.96 KN/m^2

ii) Vander Waal's Equation

$(p - a/v^2)(v - b) = RT$

$v = V/m = 1.5/5 = 0.3$

$a = 36.56$ kN m^4/(kgmol)^2

$b = 0.0428$ m^3/kg mol

after substituting we get

p = 187.48 kN/m^2

7. A mixture of gases has the following volumetric composition $CO_2 = 12\%$, $O_2 = 4\%$, $N_2 = 82\%$, $CO = 2\%$ Calculate : i)Gravimetric Composition ii)Molecular Weight of mixture iii) R of mixture

Solution:

Gas	Volume fraction(y)	Molecular Weight(M)	Product(M×y)	Mass Fraction $(x = \dfrac{M \times y}{\sum M_i y_i})$
CO_2	0.12	44	5.28	0.1755
O_2	0.04	32	1.28	0.0425
N_2	0.82	28	22.96	0.7632
CO	0.02	28	0.56	0.0186
			Total	30.08

Molecular weight of the mixture = 30.08

R of mixture = $\overline{R}/M$ = 8.314/30.18 = 0.2764 kJ/kg K

LIST OF FORMULAS:

1. $m = m_1 + m_2 + \ldots$

2. $n = n_1 + n_2 + \ldots$

3. Mass fraction $= x_i = m_i / m_{mix}$

4. Mole fraction $= y_i = n_i/n_{mix}$

5. $P_i/P = V_i/V = n_i/n = y_i$

6. $M = \sum y_i M_i$

7. $n = m/M$

8. R = $\dfrac{\overline{R}}{M}$

9. $(P - a/v^2)(v-b) = RT$

10. Z= $\dfrac{PV}{RT}$

OUTCOME: Describe ideal gas mixture composition in terms of mass fractions or mole fractions. use the Dalton model to relate pressure, volume, and temperature and to calculate changes in U , H, and S for ideal gas mixtures. Apply mass, energy, and entropy balances to systems involving ideal gas mixtures, including mixing processes.

FURTHER READING:
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- Basic and Applied Thermodynamics, P.K.Nag, 2nd Ed., Tata McGraw Hill Pub.
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