UNIT 4 IDEAL AND REAL GASES, GAS MIXTURES AND THERMODYNAMIC RELATIONS

Gas mixtures - Properties of ideal and real gases - Equations of state - Avagadro’s law- Vanderwaal’s equation of state - compressibility factor - compressibility chart - Dalton’s law of partial pressure - Exact differentials - T-ds relations - Maxwell’s relations - Clausius Clapeyron equations - Joule - Thomson coefficient.

4.1 THE CHARACTERISTIC EQUATION OF STATE

At temperatures that are considerably in excess of critical temperature of a fluid, and also at very low pressure, the vapour of fluid tends to obey the equation

$$\frac{pV}{T} = \text{constant} = R$$

In practice, no gas obeys this law rigidly, but many gases tend towards it. An imaginary ideal gas which obeys this law is called a perfect gas, and the equation $pV / T = R$, is called the characteristic equation of a state of a perfect gas. The constant $R$ is called the gas constant. Each perfect gas has a different gas constant.

Units of $R$ are Nm/kg K or kJ/kg K.

Usually, the characteristic equation is written as $pV = RT$ or for m kg, occupying V m$^3$ $pV = mRT$ ...

The characteristic equation in another form, can be derived by using kilogram-mole as a unit.

The kilogram-mole is defined as a quantity of a gas equivalent to M kg of the gas, where M is the molecular weight of the gas (e.g., since the molecular weight of oxygen is 32, then 1 kg mole of oxygen is equivalent to 32 kg of oxygen).

As per definition of the kilogram-mole, for m kg of a gas, we have $m = nM$

where $n = \text{number of moles}$. Substituting for $m$ from eqn. gives

$$pV = nMRT$$

According to Avogadro’s hypothesis the volume of 1 mole of any gas is the same as the volume of 1 mole of any other gas, when the gases are at the same temperature and pressure.

Therefore, $V/n$ is the same for all gases at the same value of $p$ and $T$. That is the quantity $pV/nT$ is a constant for all gases. This constant is called universal gas constant, and is given the symbol, $R_0$.

i.e., $MR = R_0 = pV/nT$ or $pV = nR_0T$.

Since $MR = R_0$, then $R = R_0 / M$

It has been found experimentally that the volume of 1 mole of any perfect gas at 1 bar and 0°C is approximately 22.71 m$^3$. Therefore from eqn.
R₀ = pV / nT = 1 \times 10^5 \times 22.71 / 1 \times 273.15 = 8314.3 \text{ Nm/mole K}

Using eqn. the gas constant for any gas can be found when the molecular weight is known.

4.2 VAN DER WAALS’ EQUATION

Van der Waals’ equation (for a real gas) may be written as:

\[
\left( p + \frac{a}{v^2} \right) (v - b) = RT
\]

The constants \(a\) and \(b\) are specific constants and depend upon the type of the fluid considered, \(v\) represents the volume per unit mass and \(R\) is the gas constant.

If the volume of one mole is considered then the above equation can be written as

\[
\left( p + \frac{a}{v^2} \right) (\bar{v} - b) = R₀T
\]

The units of \(p\), \(v\), \(T\), \(R\), \(a\) and \(b\) are as follows: \(p\) (Nm²), \(v\) (m³/kg-mol), \(T\) (K) and \(R = 8314 \text{ Nm/kg mol K}\), \(a\) [Nm⁴/(kg-mol)²], \(b\) (m³/kgmol).

### Constants of Van der Waals’ Equation

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Substance</th>
<th>(a) [Nm⁴/(kg-mol)²]</th>
<th>(b) [m³/kg-mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Hydrogen (H₂)</td>
<td>25105</td>
<td>0.0262</td>
</tr>
<tr>
<td>2.</td>
<td>Oxygen (O₂)</td>
<td>138250</td>
<td>0.0314</td>
</tr>
<tr>
<td>3.</td>
<td>Carbon dioxide (CO₂)</td>
<td>362850</td>
<td>0.0423</td>
</tr>
<tr>
<td>4.</td>
<td>Helium (He)</td>
<td>3417820</td>
<td>0.0228</td>
</tr>
<tr>
<td>5.</td>
<td>Air</td>
<td>135522</td>
<td>0.0362</td>
</tr>
<tr>
<td>6.</td>
<td>Water (H₂O) vapour</td>
<td>551130</td>
<td>0.0300</td>
</tr>
<tr>
<td>7.</td>
<td>Mercury (Hg) vapour</td>
<td>2031940</td>
<td>0.0657</td>
</tr>
</tbody>
</table>

4.3 REDUCED PROPERTIES

The ratios of pressure, temperature and specific volume of a real gas to the corresponding critical values are called the reduced properties.

\[
p_r = \frac{p}{p_c}, \quad T_r = \frac{T}{T_c}, \quad \nu_r = \frac{\nu}{\nu_c}
\]

4.4 LAW OF CORRESPONDING STATES

If any two gases have equal values of reduced pressure and reduced temperature, then they have same values of reduced volume; i.e., \(\nu_r = f(T_r, p_r)\) for all gases and the function is the same. This law is most accurate in the vicinity of the critical point.
4.5 COMPRESSIBILITY CHART

The compressibility factor \( Z \) of any gas is a function of only two properties, usually temperature and pressure, so that \( Z = f(Tr, pr) \) except near the critical point. 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 general compressibility chart is plotted with \( Z \) versus \( pr \) for various values of \( Tr \). This is constructed by plotting the known data of one or more gases and can be used for any gas. Such a chart is shown in Fig. 8.10. This chart gives best results for the regions well removed from the critical state for all gases.

![Generalized Compressibility Chart](image)

4.6 DALTON’S LAW

The pressure of a mixture of gases is equal to the sum of the partial pressures of the constituents. The partial pressure of each constituent is that pressure which the gas would exert if it occupied alone that volume occupied by the mixtures at the same temperature.

By the consideration of mass, \( m = m_A + m_B \)

By Dalton’s law, \( p = p_A + p_B \)

Dalton’s law is based on experiment and is found to be obeyed more accurately by gas mixtures at low pressures. The law can be extended to any number of gases,

\[ m = m_A + m_B + m_C + \ldots \text{ or } m = \Sigma m_i \]

where \( m_i \) = Mass of a constituent.
Similarly \( p = p_A + p_B + p_C + \ldots \) or \( p = \Sigma p_i \) where \( p_i \) = The partial pressure of a constituent

### 4.7 GIBBS-DALTON LAW

The internal energy, enthalpy, and entropy of a gaseous mixture are respectively equal to the sums of the internal energies, enthalpies, and entropies, of the constituents.

Each constituent has that internal energy, enthalpy and entropy, which it could have if it occupied alone that volume occupied by the mixture at the temperature of the mixture.

This statement leads to the following equations:

\[
mu = m_A u_A + m_B u_B + \ldots \quad \text{or} \quad mu = \Sigma m_i u_i \ldots \text{and}
\]

\[
mh = m_A h_A + m_B h_B + \ldots \quad \text{or} \quad mh = \Sigma m_i h_i \ldots \text{and}
\]

\[
ms = m_A s_A + m_B s_B + \ldots \quad \text{or} \quad ms = \Sigma m_i s_i \ldots
\]

### 4.8 VOLUMETRIC ANALYSIS OF A GAS MIXTURE

Let us consider a volume \( V \) of a gaseous mixture at a temperature \( T \), consisting of three constituents \( A, B \) and \( C \). Let us further assume that each of the constituents is compressed to a pressure \( p \) equal to the total pressure of the mixture, and let the temperature remain constant. The partial volumes then occupied by the constituents will be \( V_A, V_B \) and \( V_C \).

\[
m = m_A + m_B + m_C = \Sigma m_i
\]

\[
p = p_A + p_B + p_C = \Sigma p_i
\]

\[
n = n_A + n_B + n_C = \Sigma n_i
\]

Now using the eqn. \( pV = mRT \), we get

\[
m_A = \frac{p_A V}{R_A T}
\]

and

\[
m_A = \frac{p_A V_A}{R_A T}
\]
Now equating the two values for $m_A$, we have

$$\frac{p_A V}{R_A T} = \frac{p V_A}{R_A T} \quad \text{i.e.,} \quad p_A V = p V_A$$

or

$$V_A = \frac{p_A}{p} V$$

In general therefore,

$$V_i = \frac{p_i}{p} V$$

i.e.,

$$\Sigma V_i = \Sigma \frac{p_i V}{p} = \frac{V}{p} \Sigma p_i$$

We know

$$p = \Sigma p_i$$

therefore,

$$\Sigma V_i = V$$

Thus, the volume of a mixture of gases is equal to the sum of the volumes of the individual constituents when each exists alone at the pressure and temperature of the mixture. This is the statement of another empirical law, the law of partial volumes, sometimes called Amagat’s law or Leduc’s law. The analysis of mixtures, often, is simplified if it is carried out in moles. The mole is given by the equation

$$n = \frac{m}{M}$$

where, $n$ = Number of moles,
$m$ = Mass of gas, and
$M$ = Molecular weight.

According to Avogadro’s law, the number of moles of any gas is proportional to the volume of the gas at a given pressure and temperature. Referring to Fig., the volume $V$ contains $n$ moles of the mixture at $p$ and $T$. In Fig., the gas $A$ occupies a volume $V_A$ at $p$ and $T$, and this volume contains $n_A$ moles. Similarly there are $n_B$ moles of gas $B$ in volume $V_B$ and $n_C$ moles of gas $C$ in volume $V_C$.

$$\Sigma V_i = V$$

$$V_A + V_B + V_C = V$$

The total number of moles in the vessel must equal the sum of the moles of the individual constituents,

$$n = n_A + n_B + n_C = \Sigma n_i$$
4.9 The Apparent Molecular Weight and Gas Constant

An apparent molecular weight is defined by the equation

\[ M = \frac{m}{n} \]

where, \( m \) = Mass of the mixture, and
\( n \) = Number of moles of mixture.

The apparent gas constant (similarly as above) is defined by the equation

\[ R = \frac{R_0}{M} \]

It can be assumed that a mixture of perfect gases obeys all the perfect gas laws. In order to determine the gas constant for the mixture in terms of the gas constants of the constituents let us consider the equation \( pV = mRT \) both for the mixture and for a constituent as follows

\[ pV = mRT \]

and

\[ p_iV = m_iR_iT \]

Then

\[ \Sigma p_iV = \Sigma m_iR_iT \]

\[ V \Sigma p_i = T \Sigma m_iR_i \]

Also

\[ p = \Sigma p_i \]

\[ pV = T \Sigma m_iR_i \]

or

\[ pV = m_iR_i \]

\[ i.e., \]

\[ mR = \Sigma m_iR_i \]

or

\[ R = \Sigma \frac{m_i}{m} R_i \]

where \( \frac{m_i}{m} \) = mass fraction of a constituent.

We know \( p_iV = n_iR_0T \), and \( V_i = p_i/p \times V \)

Combining two equations and applied to the mixture (i.e., \( pV = nR_0T \)), we have

\[ \frac{p_iV}{pV} = \frac{n_iR_0T}{nR_0T} \]

\[ \frac{p_i}{p} = \frac{n_i}{n} \]

On combining this with eqn. (9.8), we get

\[ \frac{p_i}{p} = \frac{n_i}{n} = \frac{V_i}{V} \]

This means that the molar analysis is identical with the volumetric analysis, and both are equal to the ratio of the partial pressure to the total pressure.

The apparent molecular weight can be also be determined by the following method. Let us apply characteristic equation to each constituent and to mixture, we have
Also 

\[ m = \sum m_i \]

\[ \therefore \quad \frac{pV}{RT} = \sum \frac{p_iV}{R_iT} \]

\[ \therefore \quad \frac{p}{R} = \sum \frac{p_i}{R_i} \]

Using the relation \( R = \frac{R_0}{M} \), and substituting, we have

\[ \frac{pM}{R_0} = \sum \frac{p_iM_i}{R_0} \]

or

\[ pM = \sum p_iM_i \]

i.e.,

\[ M = \sum \frac{p_i}{p} M_i \]

Also

\[ M = \sum \frac{V_i}{V} M_i \]

and

\[ M = \sum \frac{n_i}{n} M_i \]

4.10 SPECIFIC HEATS OF A GAS MIXTURE

\[ C_v = \sum \frac{n_i}{n} C_{vi} \]

\[ C_p = \sum \frac{n_i}{n} C_{pi} \]

PROBLEMS

1. The volume of a high altitude chamber is 40 m³. It is put into operation by reducing pressure from 1 bar to 0.4 bar and temperature from 25°C to 5°C. How many kg of air must be removed from the chamber during the process? Express this mass as a volume measured at 1 bar and 25°C.

Take \( R = 287 \text{ J/kg K} \) for air.

Solution. \( V_1 = 40 \text{ m}^3 \)

\[ p_1 = 1 \text{ bar} \quad T_1 = 25 + 273 = 298 \text{ K} \]

\[ V_2 = 40 \text{ m}^3 \]

\[ p_2 = 0.4 \text{ bar} \quad T_2 = 5 + 273 = 278 \text{ K} \]

kg of air to be removed:

Assuming nitrogen to be a perfect gas,
2. A vessel of capacity 3 m³ contains 1 kg mole of N₂ at 90°C. (i) Calculate pressure and the specific volume of the gas. (ii) If the ratio of specific heats is 1.4, evaluate the values of \( c_p \) and \( c_v \). (iii) Subsequently, the gas cools to the atmospheric temperature of 20°C; evaluate the final pressure of gas. (iv) Evaluate the increase in specific internal energy, the increase in specific enthalpy, increase in specific entropy and magnitude and sign of heat transfer.

**Solution.** Mass of \( N_2 \), \( m = 1 \) kg mole i.e., 28 kg
Capacity of the vessel, \( V_1 = 3 \) m³
Temperature, \( T_1 = 90 + 273 = 363 \) K

(i) **Pressure** \( (p_1) \) and **specific volume** \( (v_1) \) of the gas :
Using the relation

\[
p_1V_1 = mRT_1
\]

\[
p_1 \times 3 = 28 \times \left( \frac{8314}{28} \right) \times 363
\]

\[
\therefore \quad p_1 = 1005994 \text{ J/m}^3 \text{ or } 10.06 \text{ bar.} \quad \text{(Ans.)}
\]

Specific volume,

\[
v_1 = \frac{V_1}{m} = \frac{3}{28} = 0.107 \text{ m}^3/\text{kg.} \quad \text{(Ans.)}
\]

(ii) \( c_p = ? \), \( c_v = ? \)

\[
\frac{c_p}{c_v} = 1.4 \text{ (given)} \quad \ldots (i)
\]

But

\[
c_p - c_v = R = \frac{8314}{28} \quad \ldots (ii)
\]

Solving for \( c_p \) and \( c_v \) between (i) and (ii)

\[
c_p = 1.039 \text{ kJ/kg K} \quad ; \quad c_v = 0.742 \text{ kJ/kg K.} \quad \text{(Ans.)}
\]

(iii) **Final pressure of the gas after cooling to 20°C** :

<table>
<thead>
<tr>
<th>Initially</th>
<th>After cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p_1 = 10.06 \text{ bar} )</td>
<td>( p_2 = ? )</td>
</tr>
<tr>
<td>( V_1 = 3 \text{ m}^3 )</td>
<td>( V_2 = 3 \text{ m}^3 )</td>
</tr>
<tr>
<td>( T_1 = 363 \text{ K} )</td>
<td>( T_2 = 20 + 273 = 293 \text{ K} )</td>
</tr>
</tbody>
</table>
3. A container of 3 m³ capacity contains 10 kg of CO₂ at 27°C. Estimate the pressure exerted by CO₂ by using: (i) Perfect gas equation (ii) Van der Waals’ equation.

Solution. Capacity of the container, \( V = 3 \text{ m}^3 \)
Mass of CO₂, \( m = 10 \text{ kg} \)
Temperature of CO₂, \( T = 27 + 273 = 300 \text{ K} \)
Pressure exerted by CO₂, \( p \):

(i) Using perfect gas equation:

Characteristic gas constant, \( R = \frac{R_0}{M} = \frac{8314}{44} = 188.95 \text{ Nm/kg K (for CO}_2\))

Using perfect gas equation

\[ pV = mRT \]

\[ p = \frac{mRT}{V} = \frac{10 \times 18895 \times 300}{3} = 188950 \text{ N/m}^2 \text{ or 1.889 bar. (Ans.)} \]

(ii) Using Van der Waals’ equation:

\[ \left( p + \frac{a}{v^2} \right)(v - b) = R_0T \]

\[ p = \frac{R_0T}{v - b} - \frac{a}{v^2} \]
4. Calculate the density of N₂ at 260 bar and 15°C by using the compressibility chart.

**Solution.**

Pressure, \( p = 260 \) bar

Temperature, \( T = 15 + 273 = 288 \) K

Density, \( \rho = ? \)

For N₂ (from Table 8.3):

\[ p_c = 38.94 \text{ bar} \]
\[ T_c = 126.2 \text{ K} \]

Now

\[ p_r = \frac{p}{p_c} = \frac{260}{38.94} = 7.6 \]

and

\[ T_r = \frac{T}{T_c} = \frac{288}{126.2} = 2.28 \]

From the compressibility chart for \( p_r = 7.6 \) and \( T_r = 2.28 \), \( Z \approx 1.03 \)

Also

\[ Z = \frac{\rho}{RT} = \frac{p}{\rho R T} \text{, where } \rho \text{ stands for density} \]

or

\[ \rho = \frac{p}{ZRT} = \frac{260 \times 10^6}{108 \times 3814 \times 288} = 281.5 \text{ kg/m}^3. \] (Ans.)

5. A vessel of 0.35 m³ capacity contains 0.4 kg of carbon monoxide (molecular weight = 28) and 1 kg of air at 20°C. Calculate: (i) The partial pressure of each constituent, (ii) The total pressure in the vessel, and (The gravimetric analysis of air is to be taken as 23.3% oxygen (molecular weight = 32) and 76.7% nitrogen (molecular weight = 28).

**Solution.**

Capacity of the vessel, \( V = 0.35 \) m³

Mass of carbon monoxide = 0.4 kg

Mass of air = 1 kg

Temperature, \( T = 20°C \) or 293 K

Mass of oxygen present in 1 kg of air = \( \frac{23.3}{100} \times 1 = 0.233 \) kg

Mass of nitrogen present in 1 kg of air = \( \frac{76.7}{100} \times 1 = 0.767 \) kg

But, characteristic gas constant,

\[ R = \frac{R_0}{M} \] ... (i)
A mixture of ideal gases consists of 4 kg of nitrogen and 6 kg of carbon dioxide at a pressure of 4 bar and a temperature of 20°C. Find: (i) The mole fraction of each constituent, (ii) The equivalent molecular weight of the mixture, (iii) The equivalent gas constant of the mixture, (iv) The partial pressures and partial volumes, (v) The volume and density of the mixture, and (vi) The cp and cv of the mixture. If the mixture is heated at constant volume to 50°C, find the changes in internal energy, enthalpy and entropy of the mixture. Find the changes in internal energy, enthalpy and entropy of the mixture if the heating is done at constant pressure. Take γ: for CO₂ = 1.286 and for N₂ = 1.4.

6. A mixture of ideal gases consists of 4 kg of nitrogen and 6 kg of carbon dioxide at a pressure of 4 bar and a temperature of 20°C. Find: (i) The mole fraction of each constituent, (ii) The equivalent molecular weight of the mixture, (iii) The equivalent gas constant of the mixture, (iv) The partial pressures and partial volumes, (v) The volume and density of the mixture, and (vi) The cp and cv of the mixture. If the mixture is heated at constant volume to 50°C, find the changes in internal energy, enthalpy and entropy of the mixture. Find the changes in internal energy, enthalpy and entropy of the mixture if the heating is done at constant pressure. Take γ: for CO₂ = 1.286 and for N₂ = 1.4.

Solution. (i) The mole fraction of each constituent:

Since mole fraction,

\[ x_i = \frac{n_i}{\Sigma n_i} \]

\[ x_{N_2} = \frac{4}{28} = \frac{4}{4 + 6} = \frac{1428}{1428 + 1364} = \frac{0.1428}{0.2792} = 0.511. \quad \text{(Ans.)} \]

\[ x_{CO_2} = \frac{6}{28} = \frac{6}{4} = \frac{1364}{1428 + 1364} = \frac{0.1364}{0.2792} = 0.488. \quad \text{(Ans.)} \]
(ii) The equivalent molecular weight of the mixture, M:

\[ M = 0.511 \times 28 + 0.488 \times 44 = 35.78 \text{ kg/kg mole.} \quad \text{(Ans.)} \]

(iii) The equivalent gas constant of the mixture, \( R_{\text{mix}} \):

Total mass, \( m = m_{N_2} + m_{CO_2} = 4 + 6 = 10 \text{ kg} \)

\[ R_{\text{mix}} = \frac{m_{N_2} R_{N_2} + m_{CO_2} R_{CO_2}}{m} \]

\[ = 4 \times \frac{8314}{28} + 6 \times \frac{8314}{44} \]

\[ = \frac{10}{0.232 \text{ kJ/kg K}.} \quad \text{(Ans.)} \]

(iv) The partial pressures and partial volumes:

\[ P_{N_2} = x_{N_2} \times p = 0.511 \times 4 = 2.044 \text{ bar.} \quad \text{(Ans.)} \]

\[ P_{CO_2} = x_{CO_2} \times p = 0.488 \times 4 = 1.952 \text{ bar.} \quad \text{(Ans.)} \]

\[ V_{N_2} = \frac{m_{N_2} R_{N_2} T}{p} = \frac{4 \times 8314 \times 293 \times 10^3}{4 \times 10^5} = 0.87 \text{ m}^3. \quad \text{(Ans.)} \]

\[ V_{CO_2} = \frac{m_{CO_2} R_{CO_2} T}{p} = \frac{6 \times 8314 \times 293 \times 10^3}{4 \times 10^5} = 0.83 \text{ m}^3. \quad \text{(Ans.)} \]

(v) The volume and density of the mixture:

Total volume of the mixture,

\[ V = \frac{mRT}{p} = \frac{m_{N_2} R_{N_2} T}{p_{N_2}} = \frac{m_{CO_2} R_{CO_2} T}{p_{CO_2}} \]

\[ = \frac{10 \times 0.232 \times 293 \times 10^3}{4 \times 10^5} = 1.699 \text{ m}^3. \quad \text{(Ans.)} \]

Density of the mixture,

\[ \rho_{\text{mix}} = \frac{P_{N_2} + P_{CO_2}}{m} = \frac{10}{1.699} = 5.88 \text{ kg/m}^3. \quad \text{(Ans.)} \]

(vi) \( c_p \) and \( c_v \) of the mixture:

\[ c_{pN_2} - c_{CVN_2} = \frac{R_{N_2}}{\gamma - 1} \]

\[ = \frac{8314}{28(14 - 1)} = 0.742 \text{ kJ/kg K} \]

\[ \text{and} \]

\[ c_{pN_2} = 1.4 \times 0.742 = 1.039 \text{ kJ/kg K} \]

Now

\[ c_{CVCO_2} = \frac{R_{CO_2}}{\gamma - 1} = \frac{8314}{44(1286 - 1)} \]

\[ = 0.661 \text{ kJ/kg K} \]

\[ \text{and} \]

\[ c_{PVCO_2} = 1.286 \times 0.661 = 0.85 \text{ kJ/kg K} \]

For the mixture:

\[ c_p = \frac{m_{N_2} c_{pN_2} + m_{CO_2} c_{pCO_2}}{m_{N_2} + m_{CO_2}} \]

\[ = \frac{4 \times 1.039 + 6 \times 0.85}{(4 + 6)} = 0.925 \text{ kJ/kg K.} \quad \text{(Ans.)} \]
7. Following is the gravimetric analysis of air:

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>23.14</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>75.53</td>
</tr>
<tr>
<td>Argon</td>
<td>1.28</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Calculate the analysis by volume and the partial pressure of each constituent when the total pressure is 1 bar.

**Solution.** We know that the analysis by volume $V_i/V$, is the same as the mole fraction $n_i/n$. Also $n_i = m_i/M_i$; therefore considering 1 kg of mixture and using a tabular method, we have

<table>
<thead>
<tr>
<th>Constituent</th>
<th>$m_i$</th>
<th>$M_i$</th>
<th>$n_i = m_i/M_i$</th>
<th>$\frac{n_i}{n} \times 100$% = $\frac{V_i}{V} \times 100$%</th>
<th>(Ans.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>0.2314</td>
<td>32</td>
<td>0.00723</td>
<td>$0.00723 \times 100 = 0.003453 = 20.94%$.</td>
<td>(Ans.)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.7553</td>
<td>28</td>
<td>0.02697</td>
<td>$0.02697 \times 100 = 0.003453 = 78.19%$.</td>
<td>(Ans.)</td>
</tr>
<tr>
<td>Argon</td>
<td>0.0128</td>
<td>40</td>
<td>0.00032</td>
<td>$0.00032 \times 100 = 0.003453 = -0.92%$.</td>
<td>(Ans.)</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.0005</td>
<td>44</td>
<td>0.00001</td>
<td>$0.00001 \times 100 = 0.003453 = -0.03%$.</td>
<td>(Ans.)</td>
</tr>
</tbody>
</table>

$n = \Sigma n_i = 0.03453$
Also, \[ \frac{p_i}{p} = \frac{v_i}{v} = \frac{n_i}{n} \]

\[ p_i = \frac{n_i}{n} \text{ hence} \]

For O₂, \[ p_{O_2} = 0.2094 \times 1 = 0.2094 \text{ bar. (Ans.)} \]
For N₂, \[ p_{N_2} = 0.7810 \times 1 = 0.7810 \text{ bar. (Ans.)} \]
For Ar, \[ p_{Ar} = 0.0093 \times 1 = 0.0093 \text{ bar. (Ans.)} \]
For CO₂, \[ p_{CO_2} = 0.0003 \times 1 = 0.0003 \text{ bar. (Ans.)} \]

4.11 FUNDAMENTALS OF PARTIAL DIFFERENTIATION

Let three variables are represented by \( x, y \) and \( z \). Their functional relationship may be expressed in the following forms:

\[ f(x, y, z) = 0 \quad \text{(i)} \]
\[ x = x(y, z) \quad \text{(ii)} \]
\[ y = y(x, z) \quad \text{(iii)} \]
\[ z = z(x, y) \quad \text{(iv)} \]

Let \( x \) is a function of two independent variables \( y \) and \( z \)
\[ x = x(y, z) \]

Then the differential of the dependent variable \( x \) is given by
\[ dx = \left( \frac{\partial x}{\partial y} \right)_z dy + \left( \frac{\partial x}{\partial z} \right)_y dz \]

where \( dx \) is called an exact differential.

If \( \left( \frac{\partial x}{\partial y} \right)_z = M \) and \( \left( \frac{\partial x}{\partial z} \right)_y = N \)

Then \[ dx = M dy + N dz \]

Partial differentiation of \( M \) and \( N \) with respect to \( z \) and \( y \), respectively, gives
\[ \frac{\partial M}{\partial z} = \frac{\partial^2 x}{\partial y \partial z} \quad \text{and} \quad \frac{\partial N}{\partial y} = \frac{\partial^2 x}{\partial z \partial y} \]
or
\[ \frac{\partial M}{\partial z} = \frac{\partial N}{\partial y} \]

\( dx \) is a perfect differential when eqn. (7.4) is satisfied for any function \( x \).

Similarly if \( y = y(x, z) \) and \( z = z(x, y) \)
then from these two relations, we have
\[ dy = \left( \frac{\partial y}{\partial x} \right)_z dx + \left( \frac{\partial y}{\partial z} \right)_x dz \]
\[ dz = \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy \]

\[ dy = \left( \frac{\partial y}{\partial x} \right)_z dx + \left( \frac{\partial y}{\partial z} \right)_x \left[ \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial z}{\partial y} \right)_x dy \right] \]

\[ = \left( \frac{\partial y}{\partial x} \right)_z + \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y dx + \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial y} \right)_x dy \]

\[ = \left( \frac{\partial y}{\partial x} \right)_z + \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y dx + dy \]

or

\[ \left( \frac{\partial y}{\partial x} \right)_z + \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = 0 \]

or

\[ \left( \frac{\partial y}{\partial z} \right)_x \left( \frac{\partial z}{\partial x} \right)_y = - \left( \frac{\partial y}{\partial x} \right)_z \]

or

\[ \left( \frac{\partial x}{\partial y} \right)_z \left( \frac{\partial z}{\partial x} \right)_y \left( \frac{\partial y}{\partial z} \right)_x = -1 \]

In terms of \( p, v \) and \( T \), the following relation holds good

\[ \left( \frac{\partial p}{\partial v} \right)_T \left( \frac{\partial T}{\partial p} \right)_v \left( \frac{\partial v}{\partial T} \right)_p = -1 \]

4.12 SOME GENERAL THERMODYNAMIC RELATIONS

The first law applied to a closed system undergoing a reversible process states that

\[ dQ = du + pdv \]

According to second law,

\[ ds = \frac{dQ}{T} \]

Combining these equations, we get

\[ Tds = du + pdv \]

\[ du = Tds - pdv \]

or

The properties \( h, f \) and \( g \) may also be put in terms of \( T, s, p \) and \( v \) as follows:

\[ dh = du + pdv + vdp = Tds + vdp \]

Helmholtz free energy function,

\[ df = du - Tds - sdT \]

\[ = - pdv - sdT \]

Gibb's free energy function,

\[ dg = dh - Tds - sdT = vdp - sdT \]

Each of these equations is a result of the two laws of thermodynamics.
The equations are known as Maxwell relations.

Since $du$, $dh$, $df$ and $dg$ are the exact differentials, we can express them as

$$du = \left( \frac{\partial u}{\partial s} \right)_v ds + \left( \frac{\partial u}{\partial v} \right)_s dv,$$

$$dh = \left( \frac{\partial h}{\partial s} \right)_p dp + \left( \frac{\partial h}{\partial p} \right)_s dp,$$

$$df = \left( \frac{\partial f}{\partial v} \right)_T dv + \left( \frac{\partial f}{\partial T} \right)_v dT,$$

$$dg = \left( \frac{\partial g}{\partial p} \right)_T dp + \left( \frac{\partial g}{\partial T} \right)_p dT.$$

Comparing these equations with (7.10) to (7.13) we may equate the corresponding co-efficients. For example, from the two equations for $du$, we have

$$\left( \frac{\partial u}{\partial s} \right)_v = T \quad \text{and} \quad \left. \frac{\partial u}{\partial v} \right|_s = -p.$$

The complete group of such relations may be summarised as follows:

$$\left( \frac{\partial u}{\partial s} \right)_v = T = \left( \frac{\partial h}{\partial s} \right)_p,$$

$$\left( \frac{\partial u}{\partial v} \right)_s = -p = \left( \frac{\partial f}{\partial v} \right)_T,$$

$$\left( \frac{\partial h}{\partial p} \right)_s = v = \left( \frac{\partial g}{\partial p} \right)_T,$$

$$\left( \frac{\partial f}{\partial T} \right)_v = -s = \left( \frac{\partial g}{\partial T} \right)_p.$$

Also,

$$\left( \frac{\partial T}{\partial v} \right)_s = - \left( \frac{\partial p}{\partial s} \right)_v,$$

$$\left( \frac{\partial T}{\partial p} \right)_s = \left( \frac{\partial v}{\partial s} \right)_p,$$

$$\left( \frac{\partial p}{\partial T} \right)_v = \left( \frac{\partial s}{\partial v} \right)_T,$$

$$\left( \frac{\partial v}{\partial T} \right)_p = - \left( \frac{\partial s}{\partial p} \right)_T.$$

The equations are known as Maxwell relations.
4.13 ENTROPY EQUATIONS (Tds Equations)

Since entropy may be expressed as a function of any other two properties, e.g., temperature $T$ and specific volume $v$,

$$ s = f(T, v) $$

i.e.,

$$ ds = \left( \frac{\partial s}{\partial T} \right)_v dT + \left( \frac{\partial s}{\partial v} \right)_T dv $$

or

$$ Tds = T \left( \frac{\partial s}{\partial T} \right)_v dT + \left( \frac{\partial s}{\partial v} \right)_T dv $$

But for a reversible constant volume change

$$ dq = c_v (dT)_v = Tds_v $$

or

$$ c_v = T \left( \frac{\partial s}{\partial T} \right)_v $$

But,

$$ \left( \frac{\partial s}{\partial v} \right)_T = \left( \frac{\partial p}{\partial T} \right)_v $$

$$ Tds = c_v dT + T \left( \frac{\partial p}{\partial T} \right)_v dv $$

This is known as the first form of entropy equation or the first Tds equation.

Similarly, writing

$$ s = f(T, p) $$

$$ Tds = T \left( \frac{\partial s}{\partial T} \right)_p dT + T \left( \frac{\partial s}{\partial p} \right)_T dp $$

where $ c_p = T \left( \frac{\partial s}{\partial T} \right)_p $.

Also

$$ \left( \frac{\partial s}{\partial p} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_p $$

whence, substituting in eqn. (7.25)

$$ Tds = c_v dT - T \left( \frac{\partial v}{\partial T} \right)_p dp $$

This is known as the second form of entropy equation.
4.14 EQUATIONS FOR INTERNAL ENERGY AND ENTHALPY

(i) Let

\[ u = f(T, v) \]

\[ du = \left( \frac{\partial u}{\partial T} \right)_v dT + \left( \frac{\partial u}{\partial v} \right)_T dv \]

To evaluate \( \left( \frac{\partial u}{\partial v} \right)_T \), let \( u = f(s, v) \)

Then

\[ du = \left( \frac{\partial u}{\partial s} \right)_v ds + \left( \frac{\partial u}{\partial v} \right)_s dv \]

or

\[ \left( \frac{\partial u}{\partial v} \right)_T = \left( \frac{\partial u}{\partial s} \right)_v \left( \frac{\partial s}{\partial v} \right)_T + \left( \frac{\partial u}{\partial v} \right)_s \]

But

\[ \left( \frac{\partial u}{\partial s} \right)_v = T, \left( \frac{\partial s}{\partial v} \right)_T = \left( \frac{\partial s}{\partial T} \right)_v, \left( \frac{\partial u}{\partial s} \right)_s = -p \]

Hence

\[ \left( \frac{\partial u}{\partial v} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_v - p \]

This is sometimes called the energy equation. From equation (7.28), we get

\[ du = c_v dT + \left\{ T \left( \frac{\partial p}{\partial T} \right)_v - p \right\} dv \]

(ii) To evaluate \( dh \) we can follow similar steps as under

\[ h = f(T, p) \]

\[ dh = \left( \frac{\partial h}{\partial T} \right)_p dT + \left( \frac{\partial h}{\partial p} \right)_T dp \]

\[ = c_v dT + \left( \frac{\partial h}{\partial p} \right)_T dp \]
To find $\frac{\partial h}{\partial p}$, let $h = f(s, p)$

Then,

$$dh = \left(\frac{\partial h}{\partial s}\right)_p ds + \left(\frac{\partial h}{\partial p}\right)_s dp$$

$$\left(\frac{\partial h}{\partial p}\right)_T = \left(\frac{\partial h}{\partial s}\right)_p \left(\frac{\partial s}{\partial p}\right)_T + \left(\frac{\partial h}{\partial p}\right)_s$$

But

$$\left(\frac{\partial h}{\partial s}\right)_p = T, \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial p}\right)_p, \left(\frac{\partial h}{\partial p}\right)_s = v$$

Hence

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T \left(\frac{\partial v}{\partial T}\right)_p$$

$$dh = c_p \, dT + \left(v - T \left(\frac{\partial v}{\partial T}\right)_p\right) dp$$

4.15 CLAUSIUS-CLAPERYON EQUATION

Clausius-Claperyon equation is a relationship between the saturation pressure, temperature, the enthalpy of evaporation, and the specific volume of the two phases involved. This equation provides a basis for calculations of properties in a two-phase region. It gives the slope of a curve separating the two phases in the p-T diagram.

![Fig.4.2 P-T Diagram](image-url)
The Clausius-Clapeyron equation can be derived in different ways. The method given below involves the use of the Maxwell relation [eqn. (7.20)]

\[
\left( \frac{dp}{dT} \right)_{v} = \left( \frac{\partial s}{\partial T} \right)_{v}
\]

Let us consider the change of state from saturated liquid to saturated vapour of a pure substance which takes place at constant temperature. During the evaporation, the pressure and temperature are independent of volume.

\[
\therefore \quad \frac{dp}{dT} = \frac{s_g - s_f}{v_g - v_f}
\]

where, \( s_g \) = Specific entropy of saturated vapour,
\( s_f \) = Specific entropy of saturated liquid,
\( v_g \) = Specific volume of saturated vapour, and
\( v_f \) = Specific volume of saturated liquid.

Also, \( s_g - s_f = s_{fg} \),
\( v_g - v_f = v_{fg} \)

where \( s_{fg} \) = Increase in specific entropy,
\( v_{fg} \) = Increase in specific volume, and
\( h_{fg} \) = Latent heat added during evaporation at saturation temperature \( T \).

\[
\therefore \quad \frac{dp}{dT} = \frac{s_{fg}}{v_{fg}} = \frac{s_{fg}}{v_{fg} \frac{h_{fg}}{T}}
\]

This is known as Clausius-Clapeyron or Clapeyron equation for evaporation of liquids.

The derivative \( \frac{dp}{dT} \) is the slope of vapour pressure versus temperature curve. Knowing this slope and the specific volume \( v_g \) and \( v_f \) from experimental data, we can determine the enthalpy of evaporation, \( (h_g - h_f) \) which is relatively difficult to measure accurately.

### 4.16 THROTTLING PROCESS AND JOULE-THOMPSON POROUS PLUG EXPERIMENT

Throttling process involves the passage of a higher pressure fluid through a narrow constriction. The effect is the reduction in pressure and increase in volume. This process is adiabatic as no heat flows from and to the system, but it is not reversible. It is not an isentropic process. The entropy of the fluid actually increases.

Such a process occurs in a flow through a porous plug, a partially closed valve and a very narrow orifice. The porous plug is shown in Fig.

![Fig. 4.3 The Joule-Thomson porous plug experiment](image)
In this system,

\[ Q = 0 \quad (\therefore \text{System is isolated}) \]
\[ W = 0 \quad (\therefore \text{There is no work interaction}) \]

![Diagram showing constant enthalpy curve](image)

Fig. 4.42. Constant enthalpy curve.

\[ \Delta PE = 0 \quad (\therefore \text{Inlet and outlet are at the same level}) \]
\[ \Delta KE = 0 \quad (\therefore \text{Kinetic energy does not change significantly}) \]

Applying the energy equation to the system

\[ h_1 = h_2 \]

This shows that \textit{enthalpy remains constant during adiabatic throttling process}.

The throttling process is commonly used for the following purposes:

(i) For determining the condition of steam (dryness fraction).

(ii) For controlling the speed of the turbine.

(iii) Used in refrigeration plant for reducing the pressure of the refrigerant before entry into the evaporator.

Throttling process frequently encountered in practice was investigated by Joule and Thompson (Lord Kelvin) in their famous \textit{porous plug experiment} (Fig. 4.41). A stream of gas at pressure \( p_1 \) and temperature \( T_1 \) is forced continuously through a \textit{porous plug} in a tube from which it emerges at a lower pressure \( p_2 \) and temperature \( T_2 \). The whole apparatus is \textit{thermally insulated}.

In this process (as earlier stated)

\[ h_1 = h_2 \]

Whether the temperature and internal energy change in a throttling process depends on whether the fluid behaves as an ideal gas or not. Since the enthalpy of an ideal gas is a function of temperature alone, it follows that
When a real gas undergoes a throttling process a change in temperature takes place. Let us perform a series of the experiments on the same gas, keeping $p_1$ and $T_1$ constant, by varying the pressure downstream of the plug to various values $p_2$, $p_3$, $p_4$ etc. After throttling let $T_1$, $T_2$, $T_3$, $T_4$ etc. be the corresponding temperatures. Now if a graph is plotted between $p$ and $T$ (Fig. 4.42), a smooth curve drawn through these points will be a curve of constant enthalpy because $h_1 = h_2 = h_3 = h_4$ etc.

It may be noted that this curve does not represent the process executed by the gas in passing through the plug, since the process is irreversible and the gas does not pass through a sequence of equilibrium states. The slope of a constant enthalpy line or a $p$-$T$ diagram at a particular state may be positive, zero or negative value. The slope is called *Joule-Thompson co-efficient*, $\mu$, and is given by

$$
\mu = \left( \frac{\partial T}{\partial p} \right)_h = 0 \text{ for ideal gas.}
$$

If we carry out other series of experiments similar to described above starting from different initial states, we can obtain a family of constant enthalpy curves as shown in Fig. 4.43. The states where $\mu = 0$ are called ‘inversion states’ and locus of these states is called the *inversion curve*.
The region inside the inversion curve is the cooling region since $\mu$ is positive, and temperature falls with fall in pressure.

The region outside the inversion curve is the heating region since $\mu$ is negative and temperature rises with fall in pressure.

Cooling can take place only if the initial temperature before throttling is below the maximum inversion temperature. This temperature is about $5T_c$.

The maximum inversion temperatures of some gases are given below:

1. $\text{He} = 24 \text{ K}$
2. $\text{H}_2 = 195 \text{ K}$
3. $\text{Air} = 603 \text{ K}$
4. $\text{N}_2 = 261 \text{ K}$
5. $\text{A} = 732 \text{ K}$
6. $\text{CO}_2 = 1500 \text{ K}$

The free expansion process is also a Joule (not Joule-Thompson). The Joule co-efficient is defined by:

$$\text{Joule co-efficient } \eta = -\left( \frac{\partial T}{\partial v} \right)_u$$

For free expansion of gases the experimental data obtained is limited. From the data available it appears that $\eta$ is positive (i.e., cooling accompanies a fall in pressure or increase in specific volume).