UNIT-IV

IDEAL AND REAL GASES, THERMODYNAMIC RELATIONS

Ideal gas

A perfect gas or an ideal gas is defined as a gas having no intermolecular forces. A gas which follows the gas laws at all ranges of pressures and temperatures can be considered as an ideal gas, but no such gas exists in nature.

Boyle’s law

Boyle’s law states that if the temperature of a gas in a closed system is maintained constant during a process, the volume of the gas will vary increasingly with absolute pressure during the change of state.

\[ V \propto \frac{1}{p} \quad \text{or} \quad pV = \text{Constant} \quad \text{when} \ T \text{ is constant} \]

Charle’s law

If the pressure of the gas in a closed system is maintained constant during a process, the volume of gas will vary directly with the absolute temperature.

\[ V \propto T \quad \text{or} \quad \frac{V}{T} = C \]

Avogadro’s law

A mole of a substance has a mass numerically equal to the molecular weight of the substance.

Example: 1 kg mole of O₂ has a mass of 32 kg
1 kg mole of N₂ has a mass of 28 kg

Avogadro’s law states that the volume of a 1 kg mole of all gases at STP (0°C and 1.01325 bar) is the same and is equal to 22.4 m³.

Example: 1 kg mole of O₂ has a mass of 32 kg and volume of 22.4 m³
1 kg mole of N₂ has a mass of 28 kg and volume of 22.4 m³

At \( p = 1.01325 \text{ bar} \) and \( T = 273.15 \text{ K} \), for 1 kg mole of gas \( V = 22.4 \text{ m}^3 \)

\[ v_m = 22.4 \text{ m}^3/\text{kg mole} \]

\[ p \times v_m = R_u T \]

\[ 1.01325 \times 10^5 \times 22.4 = R_u \times 273.15 \]

\[ R_u = 8314.3 \text{ J/kg mol K} \]

\( R_u \rightarrow \text{Universal gas constant; } v_m \rightarrow \text{Molar volume} \)

Joule’s law

This law states that there is no change of temperature when a gas expands without doing external work and without receiving or rejecting heat.

\[ u = f(T) \quad \text{only for ideal gas} \]

Equation of state

The functional relationship among the properties, pressure \( p \), molar or specific volume \( v \) and temperature \( T \), is known as an equation of state, which may be expressed in the form,

\[ f(p, v, T) = 0 \]

If two properties of a gas are known, the third can be evaluated from the equation of state.

\[ p \times v = R \times T \]

Real gas
Most of the real gases obey Boyle’s and Charle’s law at low pressures and temperatures. But the actual behaviour of real gases at elevated pressures and at low temperatures deviates considerably.

The ideal gas equation \( p v = R T \) 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 is 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.

**Van der Waals equation**

The ideal gas equation \( p v = R T \) is being used with two important assumptions, that there is little or no attraction between the two molecules of the gas and that the volume occupied by the molecules themselves is negligibly small compared to the volume of the gas. When the pressure is very small or temperature is very large, the intermolecular attraction and the volume of the molecules compared to the total volume of the gas are not of much importance, and the real gas obeys very closely the ideal gas equation. But as pressure increases, the intermolecular forces of attraction and repulsion increase, and also the volume of the molecules becomes appreciable compared to the total volume. Then the real gases deviate considerably from the ideal gas equation. Van der Waals by applying the laws of mechanics to the individual molecules, introduced two corrections terms in the ideal gas equation.

The Van der Waals equation for a real gas may be written as

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

- \( a \rightarrow \) a constant to account for the existence of mutual attraction between the molecules.
- \( a/v^2 \rightarrow \) the force of attraction
- \( b \rightarrow \) the coefficient introduced to account for the volumes of molecules, and is known as co-volume

\[
a = \frac{27 R^2 T_c^2}{64 p_c}
\]

\[
b = \frac{R T_c}{8 p_c}
\]

- \( T_c \rightarrow \) Critical temperature
- \( p_c \rightarrow \) Critical pressure

**Unique feature**
- Van der Waals equation qualitatively accounts for the heating effect observed at ordinary temperatures.

**Limitations**
- The values of \( a \) and \( b \) (which are assumed to be constant) are found to vary with temperature. Thus the results obtained from the equation are incorrect when the variation of \( a \) and \( b \) is large with respect to temperature.
- The equation is not accurate enough in the critical region.

**Virial expansions**
The virial expansion, also called the virial equation of state, is the most interesting and versatile of the equations of state for gases. The virial expansion is a power series in powers of the variable, \( \frac{B}{V} \), and has the form,

\[
\frac{pV}{RT} = A_0 + A_1 p + A_2 p^2 + A_3 p^3 + \cdots
\]

\[
\frac{pV}{RT} = B_0 + \frac{B_1}{v} + \frac{B_2}{v^2} + \frac{B_3}{v^3} + \cdots
\]

The coefficient, \( A_0, A_1, A_2, \ldots \) and \( B_0, B_1, B_2, \ldots \) are called the virial coefficients and are functions of temperature. \( A_0, B_0 \) are first virial coefficient and \( A_1, B_1 \) are second virial coefficients and so on.

**Law of corresponding states**

For each substance there is a compressibility factor. It would be very convenient if one chart could be used for all substances. The general shapes of the vapour dome and of the constant temperature lines on the \( p-v \) plane are similar for all substances, although the scales may be different. This similarity can be exploited by using dimensionless properties called ‘reduced properties’.

Reduced pressure, \( p_r = \frac{p}{p_c} \)

Reduced temperature, \( T_r = \frac{T}{T_c} \)

Reduced volume, \( v_r = \frac{v}{v_c} \)

Generally for all substances, \( v_r = f(p_r, T_r) \) and \( Z = f(p_r, T_r) \)

The relation among the reduced properties, \( p_r, T_r \) and \( v_r \) is known as the law of corresponding states.

**Compressibility**

In thermodynamics and fluid mechanics, compressibility is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change.

\[
K = \frac{1}{\nu} \frac{\partial \nu}{\partial p}
\]

where \( \nu \) is specific volume and \( p \) is pressure. The above statement is incomplete, because for any object or system the magnitude of the compressibility depends strongly on whether the process is adiabatic or isothermal. Accordingly we define the isothermal compressibility as:

\[
K_r = -\frac{1}{\nu} \left( \frac{\partial \nu}{\partial p} \right)_T
\]

where the subscript \( T \) indicates that the partial differential is to be taken at constant temperature. The adiabatic compressibility as:

\[
K_s = -\frac{1}{\nu} \left( \frac{\partial \nu}{\partial p} \right)_s
\]

where \( S \) is entropy. For a solid, the distinction between the two is usually negligible.

Coefficient of volume expansion is defined as,
\[ \beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p \]  \hspace{1cm} (4)

The inverse of the compressibility is called the bulk modulus.

We know that,
\[ \left( \frac{\partial p}{\partial v} \right)_T \left( \frac{\partial v}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_v = -1 \]  \hspace{1cm} (5)

\[ \beta v = \left( \frac{\partial v}{\partial T} \right)_p \text{ from (4)} \]

\[ -K_T v = \left( \frac{\partial v}{\partial p} \right)_T \text{ from (2)} \]

Substituting in (5),
\[ \left( \frac{-1}{K_T v} \right) \left( \beta v \right) \left( \frac{\partial T}{\partial p} \right)_v = -1 \]

\[ \frac{\beta}{K_T} = \left( \frac{\partial p}{\partial T} \right)_v \]  \hspace{1cm} (6)

Compressibility Chart

The compressibility factor \((Z)\) is used to alter the ideal gas equation to account for the real gas behaviour. The compressibility factor is usually obtained from the compressibility chart. Mathematically, it is defined as,

\[ Z = \frac{P v}{RT} = \frac{v_{actual}}{v_{ideal}} \]

\(p \rightarrow\) the pressure,

\(v \rightarrow\) the specific volume of the gas,

\(T \rightarrow\) the temperature, and
R \rightarrow \text{the gas constant.}

Z = 1 \text{ for ideal gas}

Critical compressibility factor, \( Z_c = \frac{P_c v_c}{RT_c} \)

\( Z \) can, in general, be either greater or less than unity for a real gas. The deviation from ideal gas behavior tends to become particularly significant (or, equivalently, the compressibility factor strays far from unity) near the critical point, or in the case of high pressure or low temperature. In these cases, a generalized Compressibility chart or an alternative equation of state better suited to the problem must be utilized to produce accurate results.

**Rules on partial derivatives**

**Theorem 1 (Exact differential)**

If a relation exists among the variables \( x, y \) and \( z \), then \( z \) may be expressed as function of \( x \) and \( y \).

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

Let, \( M = \left( \frac{\partial z}{\partial x} \right)_y \) and \( N = \left( \frac{\partial z}{\partial y} \right)_x \)

\[
dz = M dx + N dy
\]

Differentiating \( M \) partially with respect to \( y \), and \( N \) with respect to \( x \),

\[
\frac{\partial M}{\partial y}_x = \frac{\partial^2 z}{\partial x \partial y}
\]

\[
\frac{\partial N}{\partial x}_y = \frac{\partial^2 z}{\partial y \partial x}
\]

\[
\frac{\partial M}{\partial y}_x = \left( \frac{\partial N}{\partial x} \right)_y
\]

This is the condition of exact or perfect differential.

**Theorem 2**

If a quantity \( f \) is a function of \( x, y \) and \( z \) and a relation exists among \( x, y \) and \( z \), then \( f \) is a function of any two of \( x, y \) and \( z \).

If \( f = f(x, y, z) \)

\[
\left( \frac{\partial x}{\partial y} \right)_f \left( \frac{\partial y}{\partial z} \right)_f \left( \frac{\partial z}{\partial x} \right)_f = 1
\]

**Theorem 3**

Among the variables \( x, y \) and \( z \), any one variable may be considered as a function of the other two.

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

Among the thermodynamics variables, p, v and T, the following relation holds good.
\[
\left( \frac{\partial p}{\partial v} \right)_T \left( \frac{\partial v}{\partial T} \right)_p \left( \frac{\partial T}{\partial p} \right)_v = -1
\]

**Maxwell’s equations**

A pure substance existing in a single phase has only two independent variables. Of the eight quantities, p, v, T, s, u, h, F (Helmholtz function) and G (Gibbs function), any one may be expressed as a function of any two others.

(i) Consider a non flow process.
\[
q = w + \Delta u
dq = dw + du
du = dq – dw
= T \, ds – p \, dv
\]

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

Comparing (1) and (2)
\[
T = \left( \frac{\partial u}{\partial s} \right)_v \quad \text{and} \quad -p = \left( \frac{\partial u}{\partial v} \right)_s
\]
\[
\left( \frac{\partial T}{\partial v} \right)_s = \frac{\partial^2 u}{\partial v \partial s} \quad \text{and} \quad \left( -\frac{\partial p}{\partial s} \right)_v = \frac{\partial^2 u}{\partial s \partial v}
\]
\[
\text{But,} \quad \left( \frac{\partial^2 u}{\partial v \partial s} \right) = \left( \frac{\partial^2 u}{\partial s \partial v} \right)
\]

Therefore, \( \left( \frac{\partial T}{\partial v} \right)_s = -\left( \frac{\partial p}{\partial s} \right)_v \) \rightarrow **I – Maxwell equation**

The rate of increase in temperature with respect to volume during isentropic process is equal to the rate of decrease in pressure with respect to entropy during constant volume process.

(ii) Consider a flow process.
\[
q = w + \Delta h
dq = dw + dh
dh = dq – dw
= T \, ds + v \, dp
\]

Therefore, \( h = f(s, p) \)
\[ dh = \left( \frac{\partial h}{\partial s} \right)_p \, ds + \left( \frac{\partial h}{\partial p} \right)_s \, dp \]  

----- (2)

Comparing (1) and (2)

\[ T = \left( \frac{\partial h}{\partial s} \right)_p \quad \text{and} \quad v = \left( \frac{\partial h}{\partial p} \right)_s \]

\[ \left( \frac{\partial T}{\partial p} \right)_s = \frac{\partial^2 h}{\partial p \partial s} \quad \text{and} \quad \left( \frac{\partial v}{\partial s} \right)_p = \frac{\partial^2 h}{\partial s \partial p} \]

But,

\[ \left( \frac{\partial^2 h}{\partial p \partial s} \right) = \left( \frac{\partial^2 h}{\partial s \partial p} \right) \]

Therefore,

\[ \left( \frac{\partial T}{\partial p} \right)_s = \left( \frac{\partial v}{\partial s} \right)_p \] \rightarrow II – Maxwell equation

The rate of increase in temperature with respect to pressure during isentropic process is equal to the rate of increase in volume with respect to entropy during constant pressure process.

(iii) \[ F = u - Ts \]

\[ dF = du - (T \, ds + s \, dT) \]

\[ = du - T \, ds - s \, dT \]

But, \[ du = T \, ds - p \, dv \]

Therefore, \[ dF = T \, ds - p \, dv - T \, ds - s \, dT \]

\[ = - p \, dv - s \, dT \]  

----- (1)

Therefore, \[ F = f(v, T) \]

\[ dF = \left( \frac{\partial F}{\partial T} \right)_v \, dT + \left( \frac{\partial F}{\partial v} \right)_T \, dv \]  

----- (2)

Comparing (1) and (2)

\[ -s = \left( \frac{\partial F}{\partial T} \right)_v \quad \text{and} \quad -p = \left( \frac{\partial F}{\partial v} \right)_T \]

\[ -\left( \frac{\partial s}{\partial v} \right)_T = \frac{\partial^2 F}{\partial v \partial T} \quad \text{and} \quad -\left( \frac{\partial p}{\partial T} \right)_v = \frac{\partial^2 F}{\partial T \partial v} \]

But,

\[ \left( \frac{\partial^2 F}{\partial v \partial T} \right)_T = \left( \frac{\partial^2 F}{\partial T \partial v} \right)_v \]

Therefore,

\[ \left( \frac{\partial s}{\partial v} \right)_T = \left( \frac{\partial p}{\partial T} \right)_v \] \rightarrow III – Maxwell equation

The rate of increase in entropy with respect to volume during isothermal process is equal to the rate of increase in pressure with respect to temperature during constant volume process.

(iv) \[ g = h - Ts \]

\[ dg = dh - (T \, ds + s \, dT) \]
\[ dh - T \, ds - s \, dT \]

But, \[ dh = T \, ds + v \, dp \]

Therefore, \[ dg = T \, ds + v \, dp - T \, ds - s \, dT \]

\[ = v \, dp - s \, dT \quad -----(1) \]

Therefore, \[ g = f(p, T) \]

\[ dg = \left( \frac{\partial g}{\partial T} \right)_p \, dT + \left( \frac{\partial g}{\partial p} \right)_T \, dp \quad -----(2) \]

Comparing (1) and (2)

\[ -s = \left( \frac{\partial g}{\partial T} \right)_p \quad \text{and} \quad v = \left( \frac{\partial g}{\partial p} \right)_T \]

\[ -\left( \frac{\partial s}{\partial p} \right)_T = \frac{\partial^2 g}{\partial p \, \partial T} \quad \text{and} \quad \left( \frac{\partial v}{\partial T} \right)_p = \frac{\partial^2 g}{\partial T \, \partial p} \]

But,

\[ \left( \frac{\partial^2 g}{\partial p \, \partial T} \right)_T = \left( \frac{\partial^2 g}{\partial T \, \partial p} \right)_p \]

Therefore,

\[ \left( \frac{\partial s}{\partial p} \right)_T = -\left( \frac{\partial v}{\partial T} \right)_p \quad \Rightarrow \text{IV – Maxwell equation} \]

The rate of increase in entropy with respect to pressure during isothermal process is equal to the rate of decrease in volume with respect to temperature during constant pressure process.

**Tds equations**

(i) Let \( s = f(T, v) \Rightarrow T \) and \( v \) independent variables

\[ ds = \left( \frac{\partial s}{\partial T} \right)_v \, dT + \left( \frac{\partial s}{\partial v} \right)_T \, dv \quad -----(1) \]

Let \( u = f(T, v) \)

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

\[ = C_v \, dT + \left( \frac{\partial u}{\partial v} \right)_T \, dv \quad -----(2) \]

Also,

\[ du = T \, ds - p \, dv \quad -----(3) \]

Equating (2) and (3),

\[ T \, ds - p \, dv = C_v \, dT + \left( \frac{\partial u}{\partial v} \right)_T \, dv \]

\[ ds = \frac{C_v}{T} \, dT + \frac{1}{T} \left[ \left( \frac{\partial u}{\partial v} \right)_T + p \right] \, dv \quad -----(4) \]
Comparing (1) and (4), 
\( \left( \frac{\partial s}{\partial T} \right)_p = \frac{C_v}{T} \) \quad ----- (5)

From Maxwell III-equation, 
\( \left( \frac{\partial s}{\partial v} \right)_T = \left( \frac{\partial p}{\partial T} \right)_v \) \quad ----- (6)

Substituting (5) and (6) in (1),
\[ ds = \frac{C_v}{T} dT + \left( \frac{\partial p}{\partial T} \right)_v dv \]

\[ T \, ds = C_v dT + T \left( \frac{\partial p}{\partial T} \right)_v dv \rightarrow \text{First T ds equation} \]

We know that,
\[ \frac{\beta}{k_T} = \left( \frac{\partial p}{\partial T} \right)_v \]

\[ T \, ds = C_v dT + T \left( \frac{\beta}{k_T} \right) dv \rightarrow \text{First T ds equation} \]

(ii) Let \( s = f(T, p) \rightarrow \) \( T \) and \( p \) are independent variables

\[ ds = \left( \frac{\partial s}{\partial T} \right)_p dT + \left( \frac{\partial s}{\partial p} \right)_T dp \] \quad ----- (1)

Let \( h = f(T, p) \)

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

\[ = C_p dT + \left( \frac{\partial h}{\partial p} \right)_T dp \] \quad ----- (2)

Also, \( dh = T \, ds + v \, dp \) \quad ----- (3)

Equating (2) and (3),

\[ T \, ds + v \, dp = C_p \, dT + \left( \frac{\partial h}{\partial p} \right)_T dp \]

\[ ds = \frac{C_p}{T} dT + \frac{1}{T} \left[ \left( \frac{\partial h}{\partial p} \right)_T - v \right] dp \] \quad ----- (4)

Comparing (1) and (4), 
\( \left( \frac{\partial s}{\partial T} \right)_p = \frac{C_p}{T} \) \quad ----- (5)

From Maxwell IV-equation, 
\( \left( \frac{\partial s}{\partial p} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_p \) \quad ----- (6)

Substituting (5) and (6) in (1),
\[ ds = \frac{C_p}{T} dT - \left( \frac{\partial v}{\partial T} \right)_p dp \]

\[ T \, ds = C_p dT - T \left( \frac{\partial v}{\partial T} \right)_p dp \rightarrow \text{Second-T ds equation} \]

We know that, \( \beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p \)

\[ \beta v = \left( \frac{\partial v}{\partial T} \right)_p \]

\[ T \, ds = C_p dT - T \beta v \, dp \rightarrow \text{Second T ds equation} \]

(iii) Let \( u = f(p, v) \rightarrow p \) and \( v \) are independent variables

\[ du = \left( \frac{\partial u}{\partial p} \right)_v dp + \left( \frac{\partial u}{\partial v} \right)_p dv \] \quad \text{----- (1)}

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

\[ = C_v \frac{K_T}{\beta} \] \quad \text{----- (2)}

Also,

\[ u = h - pv \]

\[ \left( \frac{\partial u}{\partial v} \right)_p = \left( \frac{\partial h}{\partial v} \right)_p - p \]

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

\[ = C_p \frac{1}{v \beta} - p \] \quad \text{----- (3)}

Substituting (2) and (3) in (1),

\[ du = C_v \frac{K_T}{\beta} dp + \left[ \frac{C_p}{v \beta} - p \right] dv \] \quad \text{----- (4)}

We know that \( T \, ds = du + p \, dv \)

\[ T \, ds = C_v \frac{K_T}{\beta} dp + \left[ \frac{C_p}{v \beta} - p \right] dv + p \, dv \]

\[ = C_v \frac{K_T}{\beta} dp + \frac{C_p}{v \beta} dv \] \quad \text{----- (5)}
\[ T \, ds = C_v \frac{K}{\beta} \, dp + C_p \frac{1}{\beta_v} \, dv \rightarrow \text{Third } T \, ds \text{ equation} \]

Change in internal energy
\[ du = T \, ds - p \, dv \]
\[ T \, ds = C_v \, dT + T \left( \frac{\partial p}{\partial T} \right)_v \, dv \rightarrow \text{First } T \, ds \text{ equation} \]
\[ du = C_v \, dT + T \left( \frac{\partial p}{\partial T} \right)_v \, dv - p \, dv \]
\[ du = C_v \, dT + \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right] dv \]

**Internal energy of an ideal gas is function of temperature only**
\[ du = C_v \, dT + \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right] dv \]

For an ideal gas, \[ p \, v = R \, T \]
\[ p = \frac{RT}{v} \]
\[ \left( \frac{\partial p}{\partial T} \right)_v = \frac{R}{v} = \frac{p}{T} \]
\[ du = C_v \, dT + \left[ T \left( \frac{p}{T} \right)_v - p \right] dV = C_s \, dT \]

Therefore the internal energy is depending only on temperature.

**Change in internal energy when a gas obeys Van der Waals equation**

We know that, \[ du = C_v \, dT + \left[ T \left( \frac{\partial p}{\partial T} \right)_v - p \right] dv \]

Van der Waals equation is, \[ \left( p + \frac{a}{v^2} \right)(v - b) = RT \]
\[ p = \frac{RT}{v - b} - \frac{a}{v^2} \]
\[ \left( \frac{\partial p}{\partial T} \right)_v = \frac{R}{v - b} \]
Therefore,
\[ du = C_v \, dT + \left[ T \left( \frac{R}{v - b} \right) - \frac{RT}{v - b} + \frac{a}{v^2} \right] \, dv \]

\[ du = C_v \, dT + \left[ \frac{a}{v^2} \right] \, dv \]

\[ \int_1^2 du = C_v \int_1^2 dT + a \int_1^2 \frac{dv}{v^2} \]

\[ u_2 - u_1 = C_v \, (T_2 - T_1) + a \left[ \frac{1}{v_1} - \frac{1}{v_2} \right] \]

Change in entropy when a gas obeys Van der Waals equation

\[ T \, ds = C_v \, dT + T \left( \frac{\partial p}{\partial T} \right)_v \, dv \quad \text{First T ds equation} \]

\[ ds = C_v \, \frac{dT}{T} + \left( \frac{\partial p}{\partial T} \right)_v \, dv \]

Van der Waals equation is,

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

\[ p = \frac{RT}{v - b} - \frac{a}{v^2} \]

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

Therefore,

\[ ds = C_v \, \frac{dT}{T} + \left( \frac{R}{v - b} \right) \, dv \]

\[ \int_1^2 ds = C_v \int_1^2 \frac{dT}{T} + R \int_1^2 \frac{dv}{v - b} \]

\[ s_2 - s_1 = C_v \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2 - b}{v_1 - b} \right) \]

Change in enthalpy

\[ dh = T \, ds + v \, dp \]

\[ T \, ds = C_v \, dT - T \left( \frac{\partial v}{\partial T} \right)_p \, dp \quad \text{Second T ds equation} \]

\[ dh = C_v \, dT - T \left( \frac{\partial v}{\partial T} \right)_p \, dp + v \, dp \]

\[ dh = C_v \, dT - \left[ T \left( \frac{\partial v}{\partial T} \right)_p - v \right] \, dp \]
\[ dh = C_p \, dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right] dp \]

**Enthalpy of an ideal gas is function of temperature only**

\[ dh = C_p \, dT + \left[ v - T \left( \frac{\partial v}{\partial T} \right)_p \right] dp \]

For an ideal gas, \( p \, v = R \, T \)

\[ v = \frac{RT}{p} \]

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

\[ dh = C_p \, dT + \left[ v - T \left( \frac{v}{T} \right) \right] dp = C_p \, dT \]

Therefore the enthalpy is depending only on temperature.

**Difference in heat capacities \((C_p - C_v)\)**

To derive \( C_p - C_v = -T \left( \frac{\partial v}{\partial T} \right)_p^2 \left( \frac{\partial p}{\partial v} \right)_T \) or \( (C_p - C_v) = R \) or \( C_p - C_v = \frac{T \, v \, \beta^2}{K_T} \)

Note: Derive First and Second T ds equations and proceed as follows:

\[ T \, ds = C_v \, dT + T \left( \frac{\partial p}{\partial T} \right)_v \, dv \rightarrow \text{First T ds equation} \]

\[ T \, ds = C_p \, dT - T \left( \frac{\partial v}{\partial T} \right)_p \, dp \rightarrow \text{Second T ds equation} \]

Equating the above equations,

\[ C_v \, dT + T \left( \frac{\partial p}{\partial T} \right)_v \, dv = C_p \, dT - T \left( \frac{\partial v}{\partial T} \right)_p \, dp \]

\[ (C_p - C_v) \, dT = T \left( \frac{\partial p}{\partial T} \right)_v \, dv + T \left( \frac{\partial v}{\partial T} \right)_p \, dp \]

\[ dT = \left( \frac{T}{C_p - C_v} \right) \left( \frac{\partial p}{\partial T} \right)_v \, dv + \left( \frac{T}{C_p - C_v} \right) \left( \frac{\partial v}{\partial T} \right)_p \, dp \quad -----(1) \]

We can write, \( T = f(p, v) \)

\[ dT = \left( \frac{\partial T}{\partial p} \right)_v \, dp + \left( \frac{\partial T}{\partial v} \right)_p \, dv \quad -----(2) \]

Comparing (1) and (2),
\[
\left( \frac{\partial T}{\partial v} \right)_p = \frac{T}{C_p - C_v} \left( \frac{\partial p}{\partial T} \right)_v
\]  

----- (3)

From (3), \( C_p - C_v = T \left( \frac{\partial p}{\partial T} \right)_v \left( \frac{\partial v}{\partial T} \right)_p \)

----- (4)

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

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

----- (5)

Substituting (5) in (4),

\[
C_p - C_v = -T \left( \frac{\partial v}{\partial T} \right)_p^2 \left( \frac{\partial p}{\partial v} \right)_T
\]

----- (6)

\[
p v = R T
\]

\[
v = \frac{R T}{p}
\]

\[
\left( \frac{\partial v}{\partial T} \right)_p = \frac{R}{p}
\]  

----- (7)

\[
p = \frac{R T}{v}
\]

\[
\left( \frac{\partial p}{\partial T} \right)_T = - \frac{R T}{v^2}
\]  

----- (8)

Substituting (7) and (8) in (6),

\[
C_p - C_v = -T \frac{R^2}{p^2} \left( - \frac{R T}{v^2} \right) = \frac{R^3 T^2}{p^2 v^2}
\]

\[
p v = R T
\]

\[
C_p - C_v = \frac{R^3 T^2}{R^2 T^2} = R
\]

\[
C_p - C_v = R
\]  

----- (9)

We know that, \( \beta = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_p \Rightarrow \left( \frac{\partial v}{\partial T} \right)_p = \beta v \)

\[
K_r = - \frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_T \Rightarrow \left( \frac{\partial v}{\partial p} \right)_T = -v K_r
\]

Therefore equation (6) can be written as,

\[
C_p - C_v = -T \beta^2 v^2 \frac{-1}{v K_r}
\]
\[ C_p - C_v = \frac{T\nu \beta^2}{K_T} \quad \text{----- (10)} \]

**Ratio of heat capacities**

Note: Derive First and Second T ds equations and proceed as follows:

\[ T \ ds = C_v \ dT + T\left(\frac{\partial p}{\partial T}\right)_v \ dv \quad \Rightarrow \quad \text{First T } ds\text{ equation} \]

\[ T \ ds = C_p \ dT - T\left(\frac{\partial v}{\partial T}\right)_p \ dp \quad \Rightarrow \quad \text{Second T } ds\text{ equation} \]

Consider isentropic process, \( ds = 0 \)

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

\[ C_p = T\left(\frac{\partial v}{\partial T}\right)_p \ dp \]

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

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

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

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

But, \( \frac{dp}{dv} = \left(\frac{\partial p}{\partial v}\right)_T \) for isentropic process

Therefore, \[ \frac{C_p}{C_v} = \left(\frac{\partial v}{\partial T}_p \right) \left(\frac{\partial T}{\partial p}_v \right) \left(\frac{\partial p}{\partial v}_T \right) \quad \text{----- (1)} \]

We can write, \( \left(\frac{\partial p}{\partial T}_v \right) \left(\frac{\partial T}{\partial p}_v \right) \left(\frac{\partial v}{\partial v}_T \right) = -1 \)

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

Substituting in (1), \[ \frac{C_p}{C_v} = \left(\frac{\partial v}{\partial T}_p \right) \left(\frac{\partial p}{\partial p}_T \right) \quad \text{----- (2)} \]

\[ K_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p}_T \right) \Rightarrow \left(\frac{\partial v}{\partial p}_T \right) = -vK_T \]
\[ K_S = -\frac{1}{v}\left( \frac{\partial v}{\partial p} \right)_S \Rightarrow \frac{\partial v}{\partial p} \right)_S = -vK_S \]

Substituting in (2), \( \frac{C_p}{C_v} = \frac{K_T}{K_S} \) \hspace{1cm} \text{(3)}

**Joule-Thomson coefficient**

A gas is made to undergo continuous throttling process by a valve, as shown. The pressures and temperatures of the gas in the insulated pipe upstream and downstream of the valve are measured with suitable manometers and thermometers.

\[ \mu_J = \left( \frac{\partial T}{\partial p} \right)_h \]

**Joule-Thomson expansion**

Let \( p_1 \) and \( T_1 \) be the arbitrarily chosen pressure and temperature before throttling and let them be kept constant. By operating the valve manually the gas is throttled successively to different pressures and temperatures. These are then plotted on the T-p coordinates. The curve passing through all these points is an isenthalpic curve.
Isenthalpic curves and the inversion curve

The initial pressure and temperature of the gas (before throttling) are then set to new values, and by throttling to different states, a family of isenthalpes is obtained for the gas. The curve passing through the maxima of these isenthalpes is called the inversion curve.

The numerical value of the slope of an isenthalpe on a T-p diagram at any point is called the ‘Joule-Thomson coefficient’ and is denoted by $\mu_J$.

At inversion curve, $\mu_J = 0$

At right side of the inversion curve, d$T$ is positive, d$P$ is negative.

$\mu_J = -\text{ve (Heating region)}$

At left side of the inversion curve, d$T$ is negative, d$P$ is negative.

$\mu_J = +\text{ve (Cooling region)}$

$\frac{dh}{ds} = T \frac{dT}{ds} + \nu dp$  \hspace{1cm} (1)

Second $Tds$ equation is given by,

$T ds = C_p dT - T \left( \frac{\partial \nu}{\partial T} \right)_p dp$

Substituting in (1),

$dh = C_p dT - T \left( \frac{\partial \nu}{\partial T} \right)_p dp + \nu dp$

$\quad = C_p dT - \left[ T \left( \frac{\partial \nu}{\partial T} \right)_p - \nu \right] dp$

The second term in the above equation stands only for a real gas, because for an ideal gas,

$dh = C_p dT$

$dh = 0$ for isenthalpic process
Therefore,  
\[ C_p dT - \left[ T \left( \frac{\partial v}{\partial T} \right)_p \right] dp = 0 \]

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

\[ \frac{dT}{dp} = \frac{1}{C_p} \left[ T \left( \frac{\partial v}{\partial T} \right)_p \right] \]

\[ \left( \frac{\partial T}{\partial p} \right)_h = \frac{1}{C_p} \left[ T \left( \frac{\partial v}{\partial T} \right)_p \right] \]

Therefore,  
\[ \mu_j = \left( \frac{\partial T}{\partial p} \right)_h = \frac{1}{C_p} \left[ T \left( \frac{\partial v}{\partial T} \right)_p \right] \]

For an ideal gas

\[ p v = R T \]

\[ v = \frac{RT}{v} \]

\[ \left( \frac{\partial v}{\partial T} \right)_p = \frac{R}{p} = \frac{v}{T} \]

\[ \mu_j = \left( \frac{\partial T}{\partial p} \right)_h = \frac{1}{C_p} \left[ T \left( \frac{v}{T} \right) \right] = 0 \]

There is no change in temperature when an ideal gas is made to undergo a throttling.

Another form

\[ \mu_j = \left( \frac{\partial T}{\partial p} \right)_h = \frac{1}{C_p} \left[ T \left( \frac{\partial v}{\partial T} \right)_p \right] \]

But,  
\[ \beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \]

\[ \mu_j = \frac{1}{C_p} \left[ T \beta v - v \right] = \frac{v}{C_p} \left[ T \beta - 1 \right] \]

\[ \beta = \frac{1}{T} \text{ for an ideal gas since } \mu_j = 0 \]

**Clausius-Clapeyron equation**

Clausius-Clapeyron 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.
Let us consider then 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.

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

\[
\left( \frac{dp}{dT} \right) = \left( \frac{ds}{dv} \right) = \frac{s_g - s_f}{v_g - v_f} = \frac{s_{fg}}{v_{fg}}
\]

\(s_g\) = specific entropy of saturated vapour
\(s_f\) = specific entropy of saturated liquid
\(v_g\) = specific volume of saturated vapour
\(v_f\) = specific volume of saturated liquid
\(h_{fg}\) = increase in specific entropy
\(v_{fg}\) = increase in specific volume

Also,
\[
\left( \frac{dp}{dT} \right) = \frac{s_g - s_f}{v_g - v_f} = \frac{h_{fg}}{v_{fg} - v_f} = \frac{h_{fg}}{T v_{fg}}
\]

This equation is known as Clausius-Clapeyron equation for evaporation of liquids. The derivative \(dp/dT\) 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, \(h_{fg}\).