UNIT-V - GAS MIXTURES AND THERMODYNAMIC RELATIONS

Properties of ideal gas, real gas - comparison. Equations of state for ideal and real gases. Van der Waal's relation - Reduced properties - Compressibility factor - Principle of corresponding states - Generalized compressibility chart. Maxwell relations - Tds equations - heat capacities relations - Energy equation, Joule - Thompson experiment - Clausius - Clapeyron equation.

Course Objective :-

Impart knowledge on the macroscopic properties of ideal and real gases.

Course outcome :-

Apply the properties of gas mixtures in calculating the properties of gas mixtures and applying various thermodynamic relations to calculate property changes.

1. Derive the Maxwell's relation and explain their importance in thermodynamics.

Maxwell's equations relate the entropy to the three directly measurable properties such as p, v and T for pure substances (compressible).

From first law of thermodynamics,

$$Q = \Delta U + W \qquad [Q = Tds,\ W = pdv]$$

$$Tds = du + pdv \quad -①$$

W.K.T [∵ differentiation rule $d(u.v) = u.dv + v.du$]

$$h = u + pv$$

$$dh = du + d(pv) = du + p.dv + vdp$$

Substituting the value of du in this equation

$$dh = Tds - pdv + pdv + vdp$$

$$dh = Tds + vdp \quad - ②$$

By Helmhotz function,

$$a = u - Ts$$

$$da = du - T.ds - s.dT$$

Substituting the value of du in this equation

$$da = Tds - pdv - Tds - sdT$$

$$da = -pdv - sdT \quad - ③$$

By Gibb's function,

$$g = h - TS$$

$$dg = dh - Tds - sdT$$

Substituting the value of dh in this equation

$$dg = Tds + vdp - Tds - sdT$$

$$dg = vdp - sdT \quad - ④$$

W.K.T

If $z = f(x,y)$

$$dz = \left(\frac{\partial z}{\partial x}\right)_y . dx + \left(\frac{\partial z}{\partial y}\right)_x . dy$$

$$\boxed{dz = Mdx + Ndy}$$

where $M = \left(\frac{\partial z}{\partial x}\right)_y \Rightarrow \left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y \partial z} \quad - ⑤$

$N = \left(\frac{\partial z}{\partial y}\right)_x \Rightarrow \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y} \quad - ⑥$

Since ⑤ = ⑥

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

By inverse exact differential, it can be written the equation ① as

$$du = Tds - pdv$$

W.K.T $dz = Mdx + Ndy$ by comparing these equations we get

$$z = u, \ M = T, \ N = -p, \ x = s \text{ and } y = v$$

W.K.T $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

$$\boxed{\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v} \quad — ⑦$$

Similarly, the equation ② can be written as

$$dh = Tds + vdp$$

where $z = h, \ M = T, \ N = v, \ x = s$ and $y = p$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial s}\right)_p} \quad — ⑧$$

Similarly, the equation ③ can be written as

$$da = -pdv - sdT$$

where $z = a, \ M = -p, \ N = -s, \ x = v$ and $y = T$

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

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T} \quad — ⑨$$

Similarly the equation ④ can be written as

$$dg = vdp - sdT$$

where $z = g, \ M = v, \ N = -s, \ x = p$ and $y = T$

$$\boxed{\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T} \quad —— ⑩$$

These equations ⑦, ⑧, ⑨ and ⑩ are called Maxwell's equations.

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2. Derive the First and second Tds equations.

or

Derive Tds equations when

i) T and v independent

ii) T and p independent

iii) p and v independent.

or

Derive the entropy equations

or

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

Case i) Entropy as a function of T and p.

The entropy (s) of a pure substance can be expressed as a function of Temperature (T) and pressure (p).

Let $s = f(T, p)$

The exact differential

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

W.K.T

$dh = Tds + v\cancel{dp}$ [for constant pressure process $dp = 0$]

$dh = T.(ds)_p$

$mC_p(dT)_p = T.(ds)_p$ [for unit mass]

$C_p(dT)_p = T.(ds)_p \Rightarrow \frac{C_p}{T} = \left(\frac{ds}{dT}\right)_p .$

From Maxwell's fourth relation

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

Substituting the above expressions in ds equation

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

Multiply by T on both sides of the equation,

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

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

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

Case ii) Entropy as a function of T and v.

Let $s = f(T,v)$

The exact differential

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

W.K.T

$du = Tds - \cancel{pdv}^{\,0}$ [for constant volume process $dv=0$]

$mC_v(dT)_v = T(ds)_v$ [consider unit mass system]

$C_v(dT)_v = T.(ds)_v \Rightarrow \frac{C_v}{T} = \left(\frac{ds}{dT}\right)_v$

From Maxwell's third relation

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

Substituting the above expressions in the ds equation

$$ds = \frac{C_v}{T} \cdot dT + \left(\frac{\partial p}{\partial T}\right)_v \cdot dv$$

Multiply by T on both sides of the equation.

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

$$\boxed{T\,ds = C_v \cdot dT + T\left(\frac{\partial p}{\partial T}\right)_v \cdot dv}$$

It is known as the second form of entropy equation or the second Tds equation.

Case iii) Entropy as a function of p and v :-

Let $s = f(p, v)$

The exact differential

$$ds = \left(\frac{\partial s}{\partial p}\right)_v \cdot dp + \left(\frac{\partial s}{\partial v}\right)_p \cdot dv$$

This equation can be rearranged as follows.

$$ds = \left(\frac{\partial s}{\partial T}\right)_v \cdot \left(\frac{\partial T}{\partial p}\right)_v \cdot dp + \left(\frac{\partial s}{\partial T}\right)_p \cdot \left(\frac{\partial T}{\partial v}\right)_p \cdot dv$$

$$ds = \frac{C_v}{T} \cdot \left(\frac{\partial T}{\partial p}\right)_v \cdot dp + \frac{C_p}{T} \cdot \left(\frac{\partial T}{\partial v}\right)_p \cdot dv$$

multiply by T on both sides of the equation.

$$T\,ds = T \cdot \frac{C_v}{T} \cdot \left(\frac{\partial T}{\partial p}\right)_v \cdot dp + T \cdot \frac{C_p}{T} \cdot \left(\frac{\partial T}{\partial v}\right)_p \cdot dv$$

$$\boxed{T\,ds = C_v\left(\frac{\partial T}{\partial p}\right)_v \cdot dp + C_p \cdot \left(\frac{\partial T}{\partial v}\right)_p \cdot dv}$$

It is known as the third form of entropy equation or Third Tds equation.

3. Show that the internal energy of an ideal gas and an incompressible substance is a function of temperature only, $u = f(T)$.

W.K.T

from first Tds equation,

$$Tds = du + pdv$$

$$du = Tds - pdv \qquad - ①$$

Let $s = f(T, v)$

The exact differential

$$ds = \left(\frac{\partial s}{\partial T}\right)_v \cdot dT + \left(\frac{\partial s}{\partial v}\right)_T \cdot dv \qquad - ②$$

Substitute the value of ② in equation ①

$$du = T\left[\left(\frac{\partial s}{\partial T}\right)_v \cdot dT + \left(\frac{\partial s}{\partial v}\right)_T \cdot dv\right] - p.dv$$

$$du = T\left(\frac{\partial s}{\partial T}\right)_v \cdot dT + T\left(\frac{\partial s}{\partial v}\right)_T \cdot dv - pdv$$

$$du = T \cdot \frac{C_v}{T} \cdot dT + \left[T\left(\frac{\partial s}{\partial v}\right)_T - p\right] dv$$

$$\boxed{du = C_v . dT + \left[T\left(\frac{\partial p}{\partial T}\right)_v - p\right] dv} \qquad - ③$$

[From Maxwell's equation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$]

W.K.T

The ideal gas equation

$Pv = RT$ [For constant volume process]

$$(dp)_v \cdot V = R . (dT)_v$$

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{V} = \frac{P}{T}$$

Substitute the value in equation ③

$$du = C_v \cdot dT + \left[\overset{0}{\cancel{T \cdot \left(\frac{p}{T}\right) - p}} \right] dv$$

$\boxed{du = C_v \cdot dT}$ – hence for ideal gas the internal energy is a function of temperature only.

The internal energy

for ideal gas $du = C_v\, dT$

for real gas $du = C_v \cdot dT + \left[T \cdot \left(\frac{\partial p}{\partial T}\right)_v - p \right] dv$

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4. Show that the enthalpy of an ideal gas and an incompressible substance is a function of temperature only, $h = f(T)$.

W.K.T from second Tds equation

$$Tds = dh - vdp$$

$$dh = Tds + vdp \quad — ①$$

Let $s = f(T, p)$

The exact differential is

$$ds = \left(\frac{\partial s}{\partial T}\right)_p \cdot dT + \left(\frac{\partial s}{\partial p}\right)_T \cdot dp \quad — ②$$

Substitute the value of ② in equation ①

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

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

$$dh = T \cdot \frac{C_p}{T} \cdot dT + \left[T\left(\frac{\partial s}{\partial p}\right)_T + v\right] dp$$

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

$$\boxed{dh = C_p.dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp} \quad - ③$$

[From Maxwell's equation
$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$]

W.K.T

The ideal gas equation

$PV = RT$ [for constant pressure process]

$$P.(dV)_p = R.(dT)_p$$

$$\left(\frac{dv}{dT}\right)_p = \frac{R}{P} = \frac{V}{T}$$

Subsitute the above value in the equation ③

$$dh = C_p.dT + \left[\overset{0}{\cancel{v - T.\frac{v}{T}}}\right] dp$$

$\boxed{dh = C_p.dT}$ - hence it is proved that for ideal gas the enthalpy is a function of temperature only.

The enthalpy

for ideal gas $dh = C_p.dT$

for real gas $dh = C_p.dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$

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5. Prove that the difference in specific heat capacities equal to $C_p - C_v = R$ and $C_p - C_v = \frac{TV\beta^2}{K_T}$

or

From the basic principles, prove the following

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

or

Show that $C_p - C_v = R$ for an ideal gas.

The first Tds equation is given by

$$Tds = C_p\,dT - T\left(\frac{\partial v}{\partial T}\right)_p \cdot dp \qquad -①$$

Similarly, the second Tds equation is given by

$$Tds = C_v.dT + T\left(\frac{\partial p}{\partial T}\right)_v \cdot dv \qquad -②$$

Equating these two Tds equations.

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

$$C_p dT - C_v.dT = T\left(\frac{\partial p}{\partial T}\right)_v \cdot dv + T\left(\frac{\partial v}{\partial T}\right)_p \cdot dp$$

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

$$dT = \frac{T}{(C_p - C_v)} \cdot \left(\frac{\partial p}{\partial T}\right)_v \cdot dv + \frac{T}{(C_p - C_v)} \cdot \left(\frac{\partial v}{\partial T}\right)_p \cdot dp \qquad -③$$

from ideal gas equation it can be written as

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

The exact differential

$$dT = \left(\frac{\partial T}{\partial p}\right)_v \cdot dp + \left(\frac{\partial T}{\partial v}\right)_p \cdot dv \qquad -④$$

Comparing the co-efficients of dv and dp in equations ③ and ④ it can be written as.

$$\left(\frac{\partial T}{\partial p}\right)_v = \frac{T}{(C_p - C_v)} \cdot \left(\frac{\partial v}{\partial T}\right)_p$$

$$(C_p - C_v) = T \cdot \left(\frac{\partial v}{\partial T}\right)_p \cdot \left(\frac{\partial p}{\partial T}\right)_v$$

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

[if $f(x,y,z) \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$

|||ly

$$f(P,V,T) \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V = -1$$

$$\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot \frac{1}{\left(\frac{\partial P}{\partial T}\right)_V} = -1$$

$$\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V \quad]$$

$$\boxed{C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T} \quad - ⑤$$

W.K.T

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \beta V = \left(\frac{\partial V}{\partial T}\right)_P$$

|||ly

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \Rightarrow -KV = \left(\frac{\partial V}{\partial P}\right)_T$$

Substituting the above values in the equation ⑤

$$C_p - C_v = -T \cdot (\beta V)^2 \cdot \left(\frac{1}{-KV}\right)$$

$$\boxed{C_p - C_v = \frac{T \cdot \beta^2 V}{K}} \quad - ⑥$$

For ideal gas

$$\beta = \frac{1}{T}$$

$$K = \frac{1}{P}$$

Substitute the above values in the equation ⑥

$$C_p - C_v = T \cdot \frac{1}{T^2} \cdot V \times \frac{1}{\frac{1}{P}}$$

$$C_p - C_v = \frac{pv}{T} = R$$

$$\boxed{C_p - C_v = R}$$

6. Show that the ratio of specific heats

$$\frac{C_p}{C_v} = \frac{K_T}{K_s}$$

The first Tds equation is given by

$$Tds = C_p . dT - T\left(\frac{\partial v}{\partial T}\right)_p . dp \quad -①$$

Similarly, the second Tds equation is given by

$$Tds = C_v . dT + T\left(\frac{\partial p}{\partial T}\right)_v . dv \quad -②$$

W.K.T - For ideal gas

$\frac{C_p}{C_v} = \gamma$ = adiabatic index

$PV^\gamma = C$ → In adiabatic process heat transfer is zero, the entropy remains constant, $ds = 0$

$Q = Tds = 0$ [for adiabatic process]

$$① \Rightarrow \quad C_p . (dT)_s = T\left(\frac{\partial v}{\partial T}\right)_p . (dp)_s$$

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

Hlly

$$② \Rightarrow \quad C_v (dT)_s = -T\left(\frac{\partial p}{\partial T}\right)_v . (dv)_s$$

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

$$\frac{C_p}{C_v} = \frac{T\cdot\left(\frac{\partial v}{\partial T}\right)_p\cdot\left(\frac{\partial P}{\partial T}\right)_s}{-T\left(\frac{\partial P}{\partial T}\right)_v\cdot\left(\frac{\partial v}{\partial T}\right)_s}$$

$$\frac{C_p}{C_v} = -\left(\frac{\partial v}{\partial T}\right)_p\cdot\left(\frac{\partial P}{\partial T}\right)_s\cdot\left(\frac{\partial T}{\partial v}\right)_s\cdot\left(\frac{\partial T}{\partial P}\right)_v$$

$$\frac{C_p}{C_v} = -\left(\frac{\partial v}{\partial T}\right)_p\cdot\left(\frac{\partial P}{\partial v}\right)_s\cdot\left(\frac{\partial T}{\partial P}\right)_v$$

$$\frac{C_p}{C_v} = -\left(-\frac{\partial v}{\partial P}\right)_T\cdot\left(\frac{\partial P}{\partial v}\right)_s$$

$$\frac{C_p}{C_v} = \frac{\left(\frac{\partial v}{\partial P}\right)_T}{\left(\frac{\partial v}{\partial P}\right)_s}$$

$$\boxed{\frac{C_p}{C_v} = \frac{K_T}{K_s}} \qquad \boxed{\frac{C_p}{C_v} = \frac{\text{Isothermal Compressibility}}{\text{Adiabatic Compressibility}}}$$

$$\Bigg[\ f(P,v,T) = \left(\frac{\partial P}{\partial v}\right)_T\cdot\left(\frac{\partial v}{\partial T}\right)_P\cdot\left(\frac{\partial T}{\partial P}\right)_v = -1$$

$$\left(\frac{\partial v}{\partial T}\right)_P\cdot\left(\frac{\partial T}{\partial P}\right)_v\cdot\frac{1}{\left(\frac{\partial v}{\partial P}\right)_T} = -1$$

$$\left(\frac{\partial v}{\partial T}\right)_P\cdot\left(\frac{\partial T}{\partial P}\right)_v = -\left(\frac{\partial v}{\partial P}\right)_T\ \Bigg]$$

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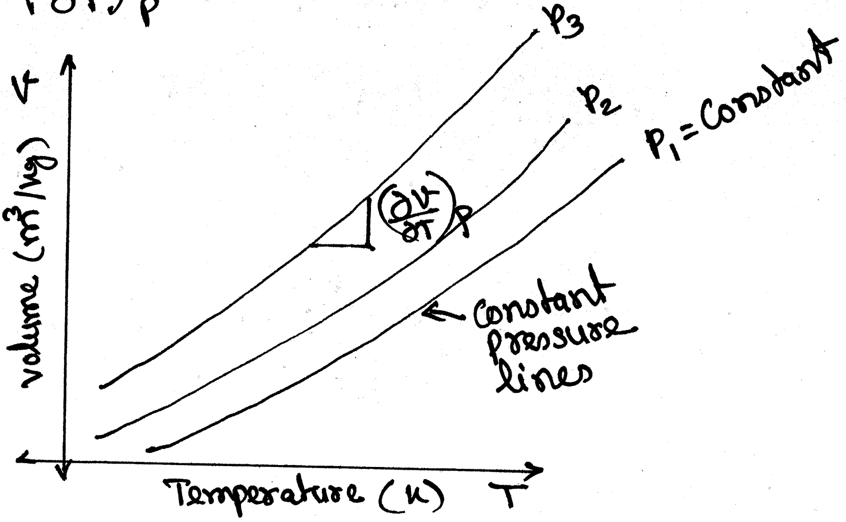
7. Explain briefly ,' Co-efficient of expansion, Isotherma compressibility, adiabatic compressibility.

Coefficient of expansion :-

Co efficient of volume expansion or expansivity is defined as the change in volume withrespect to change in temperature per unit volume at constant pressure.

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p$$



$\left(\frac{\partial v}{\partial T}\right)_p$ is called slope of the curve.

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

For ideal gas $pv = RT$ - differentiate this equation with respect to temperature at constant pressure.

$$p.(\partial v)_p = R(\partial T)_p$$

$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} = \frac{v}{T}$ Substitute the value in above equation

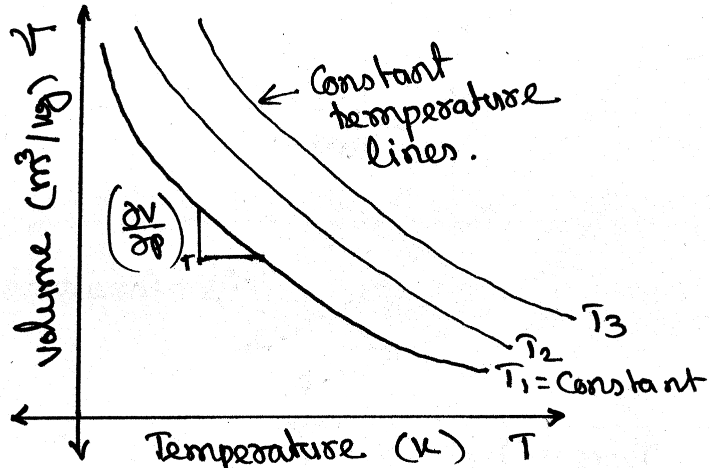
$$\beta = \frac{1}{\cancel{v}} \times \left(\frac{\cancel{v}}{T}\right) = \frac{1}{T}$$

$\beta = \frac{1}{T}$ for ideal gas

Iso thermal Compressibility :-

Iso thermal compressibility is defined as the change in volume with respect to change in pressure per unit volume at constant temperature.

$K_T = \frac{-1}{V}\left(\frac{\partial v}{\partial p}\right)_T$ negative sign indicates the p, v are indirectly proportional



$\left(\frac{\partial v}{\partial p}\right)_T$ - is called the slope of the line

$$\left(\frac{\partial v}{\partial p}\right)_T = -K_T v$$

For ideal gas

PV = RT - differentiate this equation with respect to p keeping T as constant.

$$p\cdot(\partial v)_T + v\cdot(\partial p)_T = 0$$

$$p\cdot(\partial v)_T = -v(\partial p)_T$$

$\left(\frac{\partial v}{\partial T}\right)_T = \frac{-v}{p}$ - substitute the value in above equation.

$$K_T = \cancel{-}\frac{1}{\cancel{v}}\left(\cancel{-}\frac{\cancel{v}}{p}\right) = \frac{1}{p}$$

$K_T = \frac{1}{p}$ for ideal gas.

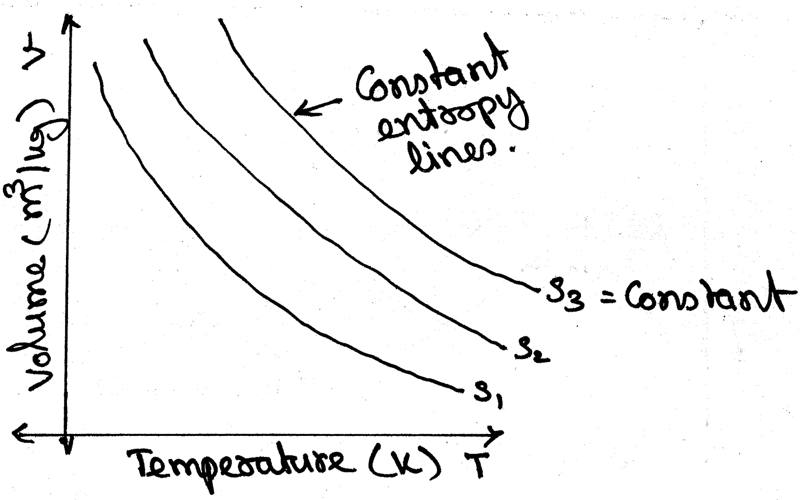
Adiabatic compressibility or Isentropic compressibility :-

Adiabatic compressibility is defined as the change in volume with respect to change in pressure per unit volume at constant entropy.

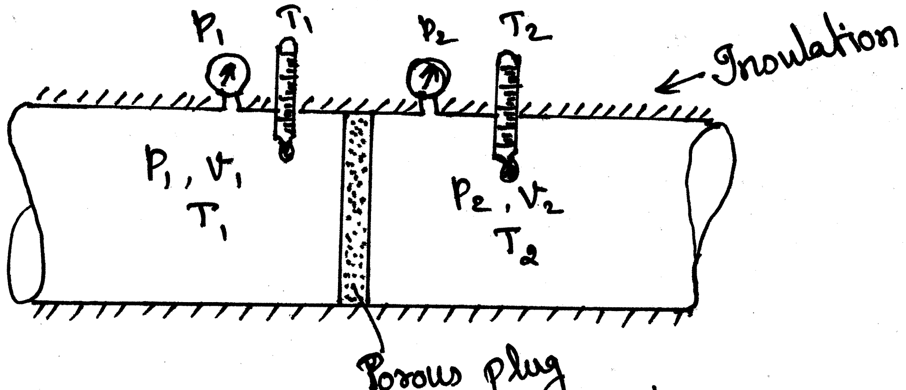
$K_s = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_s$ - the negative sign indicates that the pressure and volume are indirectly proportional.

$\left(\frac{\partial v}{\partial p}\right)_s$ - is called the slope of the curve

$$\left(\frac{\partial v}{\partial p}\right)_s = -K_s v$$



8. Explain Joule-Thompson experiment with neat sketch.



Joule-Thompson experiment.

Throttling process:-

Throttling process is defined as the fluid expansion through a minute orifice or slightly opend valve. During the throttling process, both pressure and velocity are reduced. But there is no heat transfer and no work transfer by the system. Here the enthalpy remains constant.

The Joule-kelvin effect or Joule-Thompson effect is an efficient way of cooling gases. In this a gas is made to undergo a continuous throttling process. A constant pressure is maintained at one side of a porous plug and constant lower pressure at the other side. The apparatus is thermally insulated, so heat loss can be neglected.

In the arrangement of porous plug experiment, a stream of gas at a pressure p_1 and temperature T_1, is continuously allowed to flow through a porous plug. The gas comes out from the other side of the porous plug at a pressure p_2 and Temperature T_2. The whole apparatus is completely insulated. Therefore no heat transfer takes place.

ie $Q=0$

The system does not exchange work with the surroundings.

$W=0$.

From steady flow energy equation, we know that

$$\frac{gz_1}{1000}+\frac{C_1^2}{2000}+h_1+Q=\frac{gz_2}{1000}+\frac{C_2^2}{2000}+h_2+W$$

Since there is no considerable change in velocity $C_1=C_2$ and $z_1=z_2$. Applying these conditions

$\boxed{h_1=h_2}$ Constant enthalpy or isenthalpic process.

This experiment is performed on a 'real gas' by keeping the initial pressure P_1 and Temperature T_1 constant, with various reduced down stream pressures $(P_2, P_3, \ldots\ldots)$ and the change in temperatures are noted. The results from these experiments can be plotted as a constant enthalpy curve on (T-P) plane. The slope of the constant enthalpy line is known as Joule-Thompson co-efficient. It is denoted by μ.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h.$$

Joule-Thompson co-efficent μ is defined as the change in temperature with respect to change in pressure by keeping the enthalpy constant.

For real gas, μ be canbe positive or negative or zero depending upon the thermodynamic state of the gas.

Case 1: μ is positive.

There is always a pressure drop in throttling process. So ∂P is negative. If the temperature change is also negative, the μ will be positive.

$\mu = \left(\frac{\partial T}{\partial P}\right)_h$ - This throttling process produces the cooling effect.

Case 2: μ is negative.

There is always a pressure drop in throttling process. So ∂P is negative. If the temperature change is positive, then μ will be negative.

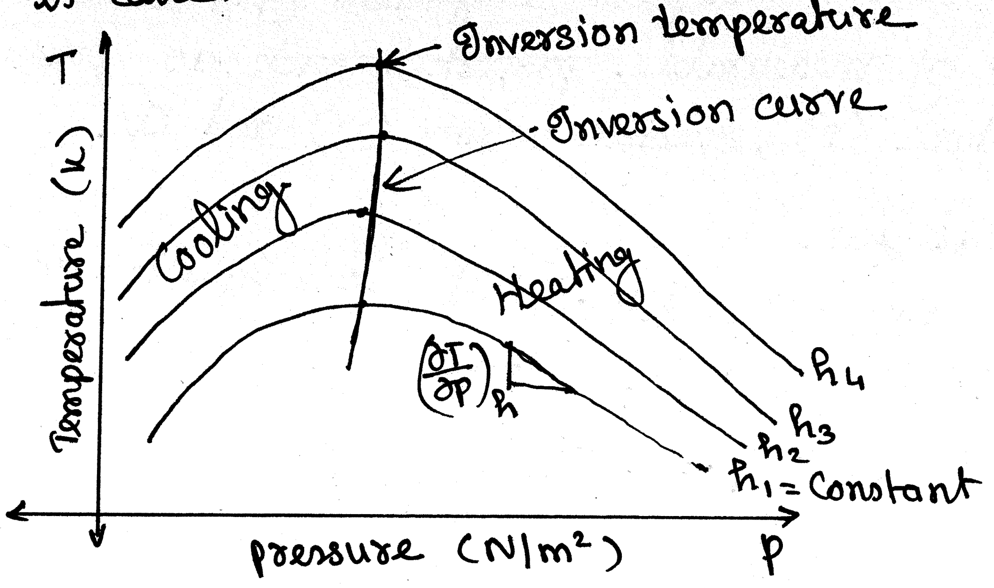
$\mu = \left(\frac{\partial T}{\partial P}\right)_h$ - This throttling process produces the heating effect.

Case 3: $\mu = 0$

When the change in temperature is zero the $\mu = 0$. The temperature at which the $\mu = 0$ is called inversion temperature for a given pressure.

Inversion Curve:-

The maximum point on each curve is called inversion point and the locus of the inversion point is called inversion curve.



A generalised equation of Joule-Thompson co-efficient can be derived by using the change of enthalpy equation.

W.K.T

$$dh = Tds + vdp$$

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

$$dh - vdp = C_p dT - T\left(\frac{\partial v}{\partial T}\right)_p.dp$$

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

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

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

Differentiating this equation with respect to pressure at constant enthalpy,

$$\left(\frac{\partial T}{\partial P}\right)_h = 0 + \frac{1}{C_p}\left[T.\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$$

The Joule - Thompson co-efficient (μ) is determined in terms of measurable properties such as pressure (P) temperature (T), specific volume (v) and C_p.

For ideal gas.

$PV = RT$ - differentiate this equation with respect to temperature keeping the pressure constant.

$$P.(\partial v)_p = R(\partial T)_p$$

$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{P} = \frac{v}{T}$ substitute the value in above equation.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_p}\left[\cancel{T}.\frac{v}{\cancel{T}} - v\right]^{0}$$

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

9. Derive the expression for Clausius - Clapeyron equation.

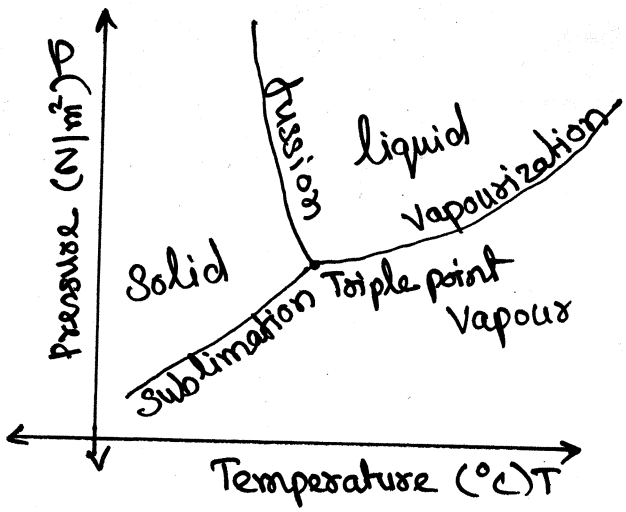
Clapeyron equation which involves the relationship between the saturation pressure, saturation temperature, the enthalpy of evaporation and the specific volume of the two phases involved. This equation provides a basis for calculation of properties in a two phase region. It gives a slope of a curve seperating the two phases in P-T diagram.

Let the entropy (s) is a function of temperature (T) and volume (v).

ie $s = f(T, v)$

The exact differential

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



When the phase is changing from saturated liquid to saturated vapour, the temperature remains constant. So the equation reduces to

$$ds = \left(\frac{\partial s}{\partial v}\right)_T \cdot dv \quad - ② \quad \left[\because dT = 0 \text{ for phase change}\right]$$

From Maxwell's relation, we know that

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$ - substituting the value in equation ②

$$ds = \left(\frac{\partial P}{\partial T}\right)_v \cdot dv$$

The term $\left(\frac{\partial P}{\partial T}\right)_v$ is the slope of the saturation curve. Integrating the above equation between saturated liquid (f) and saturated vapour (g).

$$\int_f^g ds = \int_f^g \frac{dp}{dT} . dv$$

$$[S]_f^g = \frac{dp}{dT} \int_f^g dv = \frac{dp}{dT} [V]_f^g$$

$$S_g - S_f = \frac{dp}{dT} (V_g - V_f)$$

$$\frac{dp}{dT} = \frac{S_{fg}}{V_{fg}} \quad — ③$$

From second law of thermodynamics,

W.K.T $\quad ds = \frac{dQ}{T}$

For constant pressure process

$$dQ = dh$$

$$ds = \frac{dh}{T}$$

$$S_{fg} = \frac{h_{fg}}{T} \quad - ④$$ substituting the value in equation ③

$$\boxed{\frac{dp}{dT} = \frac{h_{fg}}{T . V_{fg}}} \quad — ⑤$$

This equation is known as clausius - clapeyron equation. The above equation is valid for the change from a solid to liquid and solid to vapour.

At very low pressure $V_g = V_{fg}$ is assumed. ie $V_g \gg V_f$. So it approaches $pV = RT$. Therefore, the above equation becomes

$$\frac{dp}{dT} = \frac{h_{fg}}{T . V_g}$$

We know that the equation of state for an ideal gas

$$PV_g = RT \Rightarrow V_g = \frac{RT}{P} \rightarrow$$ substitute

this value in the equation ⑤

$$\frac{dP}{dT} = \frac{h_{fg} \times P}{T \cdot RT}$$

$$\frac{dP}{dT} = \frac{h_{fg} \cdot P}{RT^2}$$

$$\frac{dP}{P} = \frac{h_{fg}}{R} \cdot \frac{dT}{T^2}$$

Integrating the above equation.

$$\int_1^2 \frac{dP}{P} = \int_1^2 \frac{h_{fg}}{R} \cdot \frac{dT}{T^2} = \frac{h_{fg}}{R} \int_1^2 dT \cdot T^{-2}$$

$$\ln [P]_1^2 = \frac{h_{fg}}{R} \cdot \left[\frac{T^{-2+1}}{-2+1}\right]_1^2$$

$$\ln [P_2 - P_1] = \frac{h_{fg}}{R} \left[\frac{T^{-1}}{-1}\right]_1^2$$

$$\ln P_2 - \ln P_1 = \ln\left[\frac{P_2}{P_1}\right] = \frac{h_{fg}}{R} \left[-\frac{1}{T}\right]_1^2$$

$$\ln\left[\frac{P_2}{P_1}\right] = \frac{h_{fg}}{R}\left[-\frac{1}{T_2} + \frac{1}{T_1}\right]$$

$$\boxed{\ln\left[\frac{P_2}{P_1}\right] = \frac{h_{fg}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]} \quad ⑥$$

This equation is also known as clausius-clapeyron equation.

10. The latent heat of vapourization at 1 bar pressure is 2258 KJ/kg and the saturation temperature is 99.4°C. Calculate the saturation temperature at

2 bar pressure using clausius - clapeyron equation. Verify the same from the steam table data.

Given data :-

$P_1 = 1$ bar

$h_{fg} = 2258$ kJ/kg

$T_{sat} = 99.4°C = 273 + 99.4 = 372.4$ K

$P_2 = 2$ bar.

To find :-

T_{sat} at 2 bar

Sol :-

clausius - clapeyron equation $\ln\left(\frac{P_2}{P_1}\right) = \frac{h_{fg}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

$$R_{H_2O} = \frac{R_u}{M_{H_2O}} = \frac{8.314}{18} = 0.4615 \text{ kJ/kg.k}$$

$$\ln\left[\frac{2}{1}\right] = \frac{2258}{0.4615}\left[\frac{1}{372.4} - \frac{1}{T_2}\right]$$

$$0.693 = 4892.74\left[\frac{1}{372.4} - \frac{1}{T_2}\right]$$

$$1.41638 \times 10^{-4} = \left[2.685 \times 10^{-3} - \frac{1}{T_2}\right]$$

$$\frac{1}{T_2} = 2.685 \times 10^{-3} - 1.41638 \times 10^{-4}$$

$$\frac{1}{T_2} = 2.543 \times 10^{-3}$$

$$T_2 = 393.136 \text{ K} = 393.136 - 273$$

$$\boxed{T_2 = 120.136 °C}$$

from steam table at 2 bar $T_{sat} = 120.2°C$

11. Show that for a gas that obeys the law $p(v-b) = RT$, a Joule-Thompson expansion from pressure P_1 to P_2 produces a temperature change which can be found from the solution of $P_1 - P_2 = \frac{C_p}{b}(T_2 - T_1)$

Sol:-

$$p(v-b) = RT$$
$$v - b = \frac{RT}{p}$$
$$v = \frac{RT}{p} + b \quad — ①$$

Joule-Thompson co-efficient,

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_p}\left[T.\left(\frac{\partial v}{\partial T}\right)_p - v\right] \quad — ②$$

differentiating the equation ① with respect to T at Constant pressure

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p}$$ substitute the value in the equation ②

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_p}\left[T.\frac{R}{p} - v\right]$$
$$= \frac{1}{C_p}\left[\frac{RT}{p} - v\right]$$
$$= \frac{1}{C_p}\left[v - b - v\right]$$
$$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_h = \frac{-b}{C_p}} \quad — ③$$

The relation $P_1 - P_2 = \frac{C_p}{b}(T_2 - T_1)$ can be written as

$$P_2 - P_1 = -\frac{C_p}{b}(T_2 - T_1)$$

$$\frac{\partial P}{\partial T} = \frac{P_2 - P_1}{T_2 - T_1} = \frac{-C_p}{b}$$

$$\boxed{\frac{\partial T}{\partial p} = \frac{-b}{C_p}} \quad -④$$

It is inferred that the equations ③, ④ produce the same results. Hence the gas obeys the $p(v-b) = RT$.

12. Derive expressions $\left(\frac{\partial u}{\partial p}\right)_T$ and $\left(\frac{\partial h}{\partial v}\right)_T$ in terms of p, v, and T only.

Sol :- $du = Tds - pdv$

Internal energy $du = C_v . dT + T\left(\frac{\partial p}{\partial T}\right)_v . dv - pdv$ —①

differentiating the equation ① with respect to p keeping T constant.

$$\left(\frac{\partial u}{\partial p}\right)_T = 0 + T . \left(\frac{\partial p}{\partial T}\right)_v . \left(\frac{\partial v}{\partial p}\right)_T - p . \left(\frac{\partial v}{\partial p}\right)_T$$

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

Using the properties p, v, T, the cyclic relation can be expressed as.

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

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

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

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

The second Tds equation.

$$Tds = dh - vdp$$

$$dh = Tds + vdp$$

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

$$dh = C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp \quad - ②$$

differentiating each term in the equation ② with respect to v at constant T.

$$\left(\frac{\partial h}{\partial v}\right)_T = 0 + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]\left(\frac{\partial p}{\partial v}\right)_T$$

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

Using the properties p, v, T, the cyclic relation can be expressed as

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

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

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

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

---

13. One kg of ideal gas is heated from 50°C to 150°C. If R = 280 J/kg.K and $\gamma = 1.32$ for the gas, determine

1) C_p and C_v
2) change in internal energy
3) change in enthalpy
4) change in flow energy.

Given data :-

$T_1 = 50^\circ C = 50+273 = 323K$

$T_2 = 150^\circ C = 150+273 = 423K$

$R = 280 J/kg.k = 0.28 KJ/kg.k$

$\gamma = 1.32$

To find :-

$C_p, C_v, \Delta U, \Delta H, PV$

Sol :-

$C_p - C_v = R = 0.28$

$\frac{C_p}{C_v} = \gamma = 1.32 \Rightarrow C_p = 1.32 C_v$

$1.32 C_v - C_v = 0.28$

$(1.32-1) C_v = 0.28$

$C_v = \frac{0.28}{0.32} = 0.875 KJ/kg.k$

$\boxed{C_v = 0.875 KJ/kg.k}$

$C_p = 1.32 C_v = 1.32 \times 0.875$

$\boxed{C_p = 1.155 KJ/kg.k}$

change in internal energy $\Delta U = m C_v (T_2 - T_1)$

$\Delta U = 1 \times 0.875 (423-323)$

$\boxed{\Delta U = 87.5 KJ}$

change in enthalpy $\Delta H = m C_p (T_2 - T_1)$

$= 1 \times 1.155 (423-323)$

$\boxed{\Delta H = 115.5 KJ}$

Flow energy $\Delta H = \Delta U + PV$

$PV = \Delta H - \Delta U = 115.5 - 87.5$

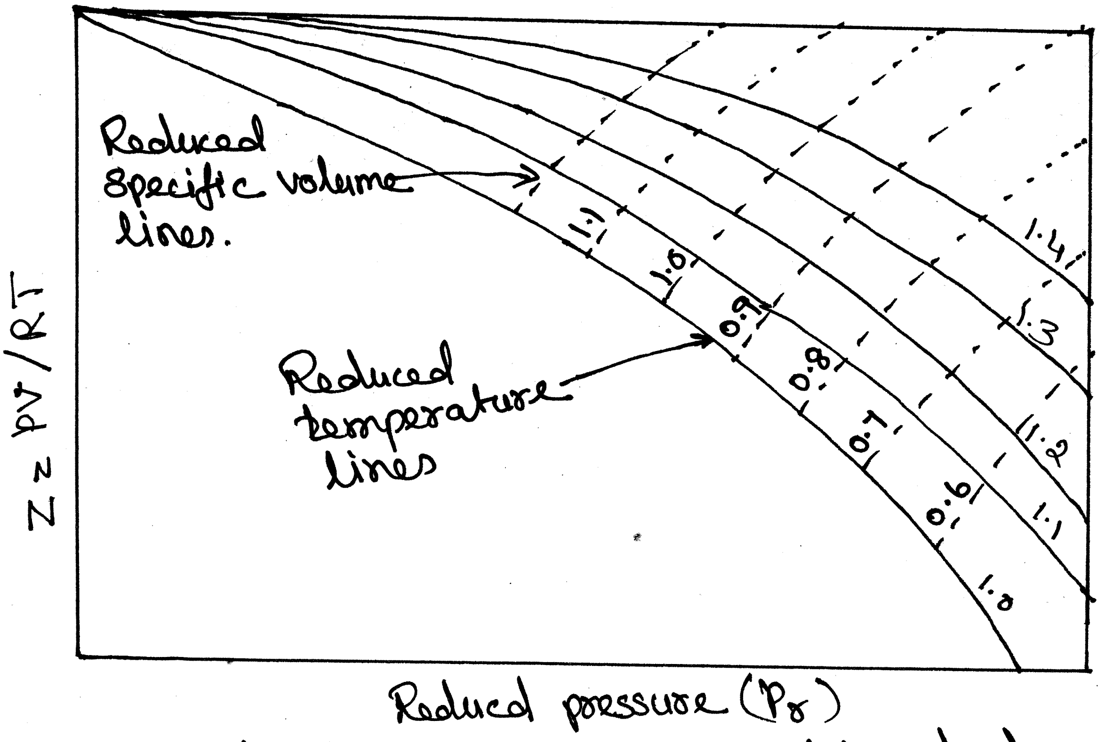
$\boxed{PV = 28 KJ}$

14. Distinguish between ideal and real gas.

Ideal Gas	Real Gas
The behaviour of ideal gas is simple.	The behaviour of real gas is complex.
Mass is considered as a "point mass". It means that the particle is extremely small where its mass is almoost zero. So it doesnot have volume.	Real gases are madeup of moleculars or atoms which occupies some space. It has a difinite volume even they are extremely small.
The collusion or impact between particles is elastic. It may be neither attractive nor repulsive energy. So there is no loss of kinetic energy.	The collusion of particles is non elastic. Since they are made up of molecules they may attract one another very strongly with the expense of repulsive energy or attractive force. Due to this there is loss in kinetic energy.
Only air is considered as ideal gas.	All gases are considered as real gas except air.
The pressure of ideal gas is more	The pressure of real gas is lesser as compared to ideal gas
It follows $pv = nRT$. This is the equation of ideal gas.	It does not follow the ideal gas equation, so the equation of real gas becomes $pv = ZRT$ or $\left(p+\frac{a}{v^2}\right)(v-b) = nRT$

15. Draw a neat schematic of a compressibility chart and indicate its salient features.

The generalised compressibility chart is the graphical plot that shows the variation of compressibility factor of any gas with the reduced pressure for various reduced temperature based on experimental data of several gases. It is a common chart applicable for all gases with limited accuracy. However, generalised compressibility chart can be used for most of the general engineering applications with reasonable accuracy.



Simple form of Compressibility chart.

In this chart, reduced pressure P_r is plotted on x axis and Z is plotted on 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 towards the right hand edge of the diagram. The dotted line curves on this diagram are the family of curves for constant ideal reduced molar volumes.

Use of compressibility chart:-

The reduced properties in the chart indicates the status of the substance from critical point.

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16. Derive the expression for equation of state for real gas

or

Derive the Van der Waal's equation for real gas.

The equation for state of ideal gas is given by

$$PV = nRT$$

In this equation it is assumed that the gas molecules does not possess any volume or the molecules have point mass. The gas molecules does not have any attractive or repulsive forces between them.

In real gas the molecules possess some volume and it is denoted by 'b'. If the gas contain 'n' number of molecules. Then the total volume is corrected to $(V-nb)$ wher b- excluded volume.

The same way each molecules will have attractive and repulsive forces between them, and the

Collision between them is not elastic in nature. So the pressure experienced by the vessel to be corrected to accomadate these forces.

Actual pressure P_{act} = Pressure recorded (p) + Attractive forces.

The attractive forces < attractive force $\propto$ density; Collision $\propto$ density

W.K.T $\quad \rho = \frac{n}{V}$

The attractive forces $= a.\frac{n}{V}.\frac{n}{V} = a.\frac{n^2}{V^2}$

where a- coefficient of attractive forces.

Now these corrections are included in the ideal gas equation.

The equation of state for real gas

$$\left(P+\frac{an^2}{V^2}\right)(V-nb) = nRT$$

If n=1 then the equation becomes

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

This equation is known as Van der Waal's equation of state for real gas.

For ideal gas, the constants a, and b are zero. The value's of a and be are dependent on the type of fluid or gases used.

The values of a and b is theoritically determined

$$a = \frac{27 R^2 (T_c)^2}{64 P_c}$$

$$b = \frac{RT_c}{8 P_c}$$

where
T_c - Critical temperature
P_c - critical pressure

The Vander Waal's equation has Some limitations as follows.

1. The study had not been made closely under actual conditions and its validity bias failed.
2. The values of a and b are assumed as constant but they will vary with temperature which is found experimentally.
3. At critical point, Van der Waal's equation becomes

$$\frac{P_c V_c}{RT_c} = \frac{3}{8} \text{ for real gases}$$

$$\frac{P_c V_c}{RT_c} = 1 \text{ for ideal gases.}$$

But, experimentally, $\frac{P_c V_c}{RT_c}$ changes from 0.2 to 0.3 for most of the gases.

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17. A vessel of volume $0.3\,m^3$ contains 15 kg of air at 303K. Determine the pressure exerted by the air using

1. Perfect gas equation

2. Van der Waal's equation

3. Generalised compressibility chart.

Take critical temperature of air is 132.8 K and critical pressure of air is 37.7 bar.

Given data:-

$V = 0.3\ m^3$ $\qquad R_{for\ air} = 0.287\ kJ/kg.K$

$m = 15\ kg$

$T = 303\ K$

$T_c = 132.8\ K$

$P_c = 37.7\ bar = 3770\ kN/m^2$

To find:-

$p = ?$

Sol:-

1. Perfect gas equation:-

$$pV = mRT$$

$$p = \frac{mRT}{V} = \frac{15 \times 0.287 \times 303}{0.3}$$

$$\boxed{p = 4348.05\ kPa}$$

2. Van der Waal's equation:-

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

$$a = \frac{27 R^2 T_c^2}{64 P_c} = \frac{27 \times (0.287)^2 (132.8)^2}{64 \times 3770}$$

$$a = 0.162$$

$$b = \frac{RT_c}{8P_c} = \frac{0.287 \times 132.8}{8 \times 3770} = 1.26 \times 10^{-3}$$

$$b = 1.26 \times 10^{-3}$$

Specific volume $v = \frac{V}{m} = \frac{0.3}{15} = 0.02\ m^3/kg$

Substituting the values of a, b, v in the equation,

$$\left(p + \frac{0.162}{(0.02)^2}\right)\left(0.02 - 1.26 \times 10^{-3}\right) = 0.287 \times 303$$

$$(p + 405)(0.01874) = 86.961$$

$$p + 404 = \frac{86.961}{0.01874} = 4640.39$$

$$p = 4640.39 - 404$$

$$\boxed{p = 4236.39\ kN/m^2}$$

3. Generalised Compressibility chart.

Reduced temperature $T_R = \frac{T}{T_c} = \frac{303}{132.8} = 2.28$

Reduced volume $V_R = \frac{V}{V_c} = \frac{V \times P_c}{RT_c} = \frac{0.02 \times 3770}{0.287 \times 132.8}$

$$V_R = 1.98\ m^3/kg.$$

The reduced temperature is 2.28 and reduced specific volume is 1.98 m^3/kg. Both intersect at one point. Mark this point on compressibility chart. From chart corresponding (Z) value is 0.99

W.K.T

Compressibility factor $Z = \frac{Pv}{RT}$

$$0.99 = \frac{P \times 0.02}{0.287 \times 303}$$

$$\boxed{P = 4304.6 \text{ KN}/m^2}$$

18. Consider an ideal gas at 303 K and 0.86 m³/kg. As a result of some disturbance the state of the gas changes to 304 K and 0.87 m³/kg. Estimate the change in pressure of the gas as a result of this disturbance.

Given data :-

$T_1 = 303K$
$v_1 = 0.86 \text{ m}^3/\text{kg}$
$T_2 = 304 \text{ K}$
$v_2 = 0.87 \text{ m}^3/\text{kg}$

To find :-

$dp = ?$

Sol :-

Ideal gas equation $P_1 v_1 = RT_1$

$$P_1 = \frac{RT_1}{v_1} = \frac{0.287 \times 303}{0.86} = 101.12 \text{ kPa}$$

|||ly $P_2 v_2 = RT_2$

$$P_2 = \frac{RT_2}{v_2} = \frac{0.287 \times 304}{0.87} = 100.285 \text{ kPa}$$

$$dP = P_1 - P_2 = 101.12 - 100.285$$

$$\boxed{dP = 0.835 \text{ kPa}}$$

UNIT-V, GAS MIXTURES AND THERMODYNAMIC RELATIONS

TWO MARK QUESTIONS AND ANSWERS

1. Define Isothermal compressibility. [OCT-95]

Isothermal compressibility is defined as the ratio of change in volume with respect to the change in pressure per unit volume by keeping the temperature constant.

$$k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

2. What is meant by Virtual expansion? [Apr-03]

Virial or Virtual expansions are only applicable to gases of low and medium densities. The equation of state of a substance is given by

$$p = \frac{RT}{V} + \frac{a(T)}{V^2} + \frac{b(T)}{V^3} + \frac{c(T)}{V^4} + \cdots\cdots$$

The co-efficients a(T), b(T), c(T) are virtual co-efficients. They will vanish when the pressure becomes zero. Then the equation of state reduces to the ideal gas equation.

3. What is co-efficient of volumatric expansion? [Apr-08]

The co-efficient of volumatric expansion is defined as the ratio of change in volume with respect to change in temperature per unit volume by keeping the the pressure Constant.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

4. What are Maxwell's equations [Nov-06, Nov-08]

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial S}\right)_V , \qquad \left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial v}{\partial S}\right)_p$$

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

5. Show that Joule-Thompson co-efficient is zero for an ideal gas [Nov-03, Apr-12]

Joule-Thompson co-efficient $\mu = \left(\frac{\partial T}{\partial p}\right)_h = \frac{1}{C_p}\left[T\left(\frac{\partial v}{\partial T}\right)_p - v\right]$

for ideal gas $PV = RT$

differentiate the above equation with respect to T by keeping the pressure (P) constant.

$$p.(\partial v)_p = R.(\partial T)_p \Rightarrow \left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} = \frac{v}{T}$$

$$\mu = \frac{1}{C_p}\left[T.\frac{v}{T} - v\right] = 0$$

$\boxed{\mu = 0}$ for ideal gases.

6. State the Van der Waal's equation for a real gas of m kg. [Nov-11]

The Van der Waal's equation for real gas is given by

$$\left(p + \frac{a}{v^2}\right)(v - b) = mRT$$

For ideal gas, the constants a, and b are zero. The values of a and b are dependent on the type of fluid or gases used.

7. What is known as the equation of state? [Dec-16]

An equation of state [EOS] is a thermodynamic expression that relates pressure [P], temperature [T] and volume [V]. This equation is used to describe the state of reservoir fluids at given conditions.

For ideal gas, the equation of state is $PV = mRT$.

8. What is meant by generalized compressibility chart? and what are its features? [May-17]

Generalized compressibility chart is a useful tool for predicting the properties of gases or gas mixtures with acceptable accuracy for most engineering purpose.

In compressibility chart, reduced pressure is on the X-axis and Z is on the Y axis with different reduced temperature graphs.

9. Define Compressibility factor. [Dec-17]

In thermodynamics, the compressibility factor (Z) also known as the compression factor or the gas deviation factor, is a correction factor which describes the deviation of a real gas from ideal gas behavior.

$$Z = \frac{PV}{RT}, \quad Z = 1 \text{ for ideal gas.}$$

10. Write down the first and second T-ds equations.

[May-18, Dec-16]

First T-ds equation $\quad T ds = C_v \cdot dT + T \cdot \left(\frac{\partial p}{\partial T}\right)_v \cdot dv$

Second T.ds equation $Tds = C_p dT - T.\left(\frac{\partial v}{\partial T}\right)_p . dp$

11. What is Joule-Thompson co-efficient? Why it is zero for an ideal gas? [May-19, May-17]

Joule-Thompson co-efficient is defined as the ratio of change of temperature with respect to pressure during an isenthalpic process or Throttling process.

Ideal gases do not show any cooling or heating because there are no intermolecular forces of attraction. For no heating or cooling Joule-Thompson co-efficient is zero.

12. What is the importance of Joule-Thompson co-efficient [Dec-19, May-16]

Joule-Thompson co-efficient gives slope of constant enthalpy lines on temperature-pressure diagram. Thus it is a parameter for characterizing the throttling process.

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h$$

If $\mu = 0$, temperature remains constant during the process.

$\mu > 0$, temperature decreases during the process - cooling effect.

$\mu < 0$, temperature increases during the process. - heating effect.