

Mathematical Tools

$z = f(x, y)$

← dependent → independent

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

$$dz = M dx + N dy$$

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

If x, y, z are point functions

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

→ path independent

$$\Rightarrow \left(\frac{\partial M}{\partial y} \right)_x = \frac{\partial^2 z}{\partial y \partial x} \Big|_x ; \left(\frac{\partial N}{\partial x} \right)_y = \frac{\partial^2 z}{\partial x \partial y} \Big|_y$$

Both are equal } As in diffⁿ order doesn't matter

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

⇒ Reciprocity Relation

$$\left(\frac{\partial x}{\partial y} \right)_p \left(\frac{\partial y}{\partial z} \right)_p \left(\frac{\partial z}{\partial x} \right)_p = 1$$

⇒ Chain Relation

Maxwell Relations

These are relations in terms of properties which are physically measurable i.e. P, V, T and S . They are used to calculate entropy of the system in terms of measurable parameters

For closed systems

$$\Rightarrow Q - W = \Delta E$$

$$dQ - dW = dE$$

$$dQ - dW = dU$$

For a simple compressible system having fixed mass and chemical composition in a piston cylinder type mechanism.

$$TdS - PdV = dU$$

$$TdS = dU + PdV$$

$$\boxed{dU = TdS - PdV} \quad \text{--- ①}$$

$$\Rightarrow H = U + PV$$

$$dH = dU + PdV + VdP$$

$$\boxed{dH = TdS + VdP} \quad \text{--- ②}$$

$$\Rightarrow G = H - TS$$

$$dG = dH - TdS - SdT$$

$$\boxed{dG = VdP - SdT} \quad \text{--- ③}$$

$\Rightarrow$ ^{Helmholtz's} $A = U - TS$

$$dA = dU - Tds - SdT$$

$$\boxed{dA = -PdV - SdT} \quad \text{--- (4)}$$

From (1) $\rightarrow U = f(S, V)$

$$dU = \left(\frac{\partial U}{\partial S}\right)_V ds + \left(\frac{\partial U}{\partial V}\right)_S dV \quad \text{--- (A)}$$

$$dZ = Mdx + Ndy$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \quad \rightarrow \text{Applying this in eq (1)}$$

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \quad \rightarrow \text{Ist Maxwell Relation}$$

Applying this in eq (2).

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \quad \rightarrow \text{IInd Maxwell Relation}$$

Applying this in eq (3).

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \quad \rightarrow \text{IIIrd Maxwell Relation}$$

Applying this in eq (4).

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T} \quad \rightarrow \text{IVth Maxwell Relation}$$

Alternative

⇒ Comparing eq ① and ④

$$T = \left(\frac{\partial U}{\partial S} \right)_V$$

$$-P = \left(\frac{\partial U}{\partial V} \right)_S \quad \left. \begin{array}{l} \text{Take diff wrt } S \text{ at} \\ \text{constant } V. \end{array} \right\}$$

Take differential wrt V at constant S .

$$\Rightarrow \left(\frac{\partial T}{\partial V} \right)_S = \frac{\partial^2 U}{\partial V \partial S} \quad \left(\frac{\partial P}{\partial S} \right)_V = \frac{\partial^2 U}{\partial S \partial V}$$

They are equal

So, $\boxed{\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V} \rightarrow \text{Ist Maxwell's equation}$

Now,

$$\Rightarrow h = f(S, P)$$

$$dh = \left(\frac{\partial h}{\partial S} \right)_P + \left(\frac{\partial h}{\partial P} \right)_S \quad \text{--- (B)}$$

Compare ② and ⑧

$$T = \left(\frac{\partial h}{\partial S} \right)_P, \quad V = \left(\frac{\partial h}{\partial P} \right)_S$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial^2 h}{\partial P \partial S} \right), \quad \left(\frac{\partial V}{\partial S} \right)_P = \left(\frac{\partial^2 h}{\partial S \partial P} \right)$$

They are equal

$$\boxed{\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P} \rightarrow \text{IInd Maxwell's equation}$$

Now,

$$\Rightarrow G = f(P, T)$$

$$dG = \left(\frac{\partial G}{\partial P} \right)_T + \left(\frac{\partial G}{\partial T} \right)_P \quad \text{--- (C)}$$

Compare (B) and (C)

$$V = \left(\frac{\partial G}{\partial P} \right)_T, \quad -S = \left(\frac{\partial G}{\partial T} \right)_P$$

$$\left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial^2 G}{\partial T \partial P} \right), \quad - \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial^2 G}{\partial P \partial T} \right)$$

They are equal

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

 $\rightarrow$ IIIrd Maxwell's equation

Now,

$$a = f(V, T)$$

$$da = \left(\frac{\partial a}{\partial V} \right)_T + \left(\frac{\partial a}{\partial T} \right)_V$$

$$-P = \left(\frac{\partial a}{\partial V} \right)_T, \quad -S = \left(\frac{\partial a}{\partial T} \right)_V$$

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\partial^2 a}{\partial T \partial V}, \quad - \left(\frac{\partial S}{\partial V} \right)_T = \frac{\partial^2 a}{\partial V \partial T}$$

They are equal

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

 $\rightarrow$ IVth Maxwell's Equation

Specific Heat at Const. Pressure (C_p)

$$\Rightarrow C_p = \left(\frac{\partial h}{\partial T} \right)_p \quad \text{--- (i)} \quad ; \quad C_v = \left(\frac{\partial u}{\partial T} \right)_v \quad \text{--- (iii)}$$

$$dh = Tds + vdp \rightarrow 0 \quad (\text{because of const. Pressure})$$

$$dh = Tds \quad \text{--- (ii)}$$

$$\text{from eq (i)} \quad C_p dT = dh$$

$$\text{from eq (i) and (ii)} \quad C_p dT = Tds$$

$$C_p = T \left(\frac{ds}{dT} \right) = \frac{dh}{dT}$$

Specific Heat at Const. Volume (C_v)

$$\Rightarrow du = Tds - PdV \rightarrow 0 \quad (\text{because of const. Volume})$$

$$du = Tds$$

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

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

$$= \frac{C_v dT}{T} + \left(\frac{\partial P}{\partial T} \right)_v dv \quad \left[\text{Using Maxwell Relation} \right]$$

Expression for
change in
entropy

$$S_2 - S_1 = \frac{1}{T} \int_1^2 C_v dT + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T} \right)_v dv$$

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

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{C_P}{T} dT + \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T} \right)_P dP$$

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

$$\Rightarrow U = f(T, v)$$

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

$$= C_v dT + \left(\frac{\partial U}{\partial v} \right)_T dv$$

— (1)

Let

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

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

— (2)

$$\left\{ dU = T dS - P dv \right\}$$

— (3)

Substitute ∂S from eq (2) into (3)

$$dU = T \left(\frac{\partial S}{\partial T} \right)_v dT + \left[T \left(\frac{\partial S}{\partial v} \right)_T - P \right] dv \quad \text{— (4)}$$

Compare (1) and (4)

$$T \left(\frac{\partial S}{\partial T} \right)_v = C_v \Rightarrow \left(\frac{\partial S}{\partial T} \right)_v = \frac{C_v}{T}$$

$$\left(\frac{\partial U}{\partial v} \right)_T = \left[T \left(\frac{\partial S}{\partial v} \right)_T - P \right] \Rightarrow \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] \left\{ \begin{array}{l} \text{Using} \\ \text{Maxwell's} \\ \text{Relation} \end{array} \right\}$$

Substitute back into eq ①

$$dU = C_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$$

$$\left\{ \begin{array}{l} U = f(T, P) \\ U = f(P, V) \end{array} \right\}$$

$$(U_2 - U_1) = \int_{T_1}^{T_2} C_v dT + \int_{v_1}^{v_2} \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$$

$$\Rightarrow h = f(T, P)$$

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP$$

$$= C_p dT + \left(\frac{\partial h}{\partial P} \right)_T dP \quad - \text{①}$$

$$\text{Let } S = f(T, P)$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad - \text{②}$$

$$dh = T dS + v dP \quad - \text{③}$$

Substitute dS from eq ② and ③

$$dh = T \left(\frac{\partial S}{\partial T} \right)_P dT + \left[T \left(\frac{\partial S}{\partial P} \right)_T + v \right] dP \quad - \text{④}$$

Compare ① and ④

$$T \left(\frac{\partial S}{\partial T} \right)_P = C_p \Rightarrow \left(\frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T}$$

$$\left(\frac{\partial h}{\partial P} \right)_T = \left[T \left(\frac{\partial S}{\partial P} \right)_T + v \right]$$

$$= \left[-T \left(\frac{\partial v}{\partial T} \right)_P + v \right] \text{ using Maxwell's Relation}$$

Substituting back into eq ①

$$dh = c_p dT + \int_P \left[-T \left(\frac{\partial v}{\partial T} \right)_P + v \right] dP$$

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} \left[-T \left(\frac{\partial v}{\partial T} \right)_P + v \right] dP$$

While solving the practical problems we need only to determine either $u_2 - u_1$ or $h_2 - h_1$ - - -

- - - depending upon which is more suitable to the experimental data. The other can easily be determined by using the definition of enthalpy.

$$h = u + Pv$$

$$h_2 - h_1 = (u_2 - u_1) + (P_2 v_2 - P_1 v_1)$$

Volume Expansivity (β)

Defined as change in volume with change in temperature keeping pressure constant

Also known as coefficient of volume expansion

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

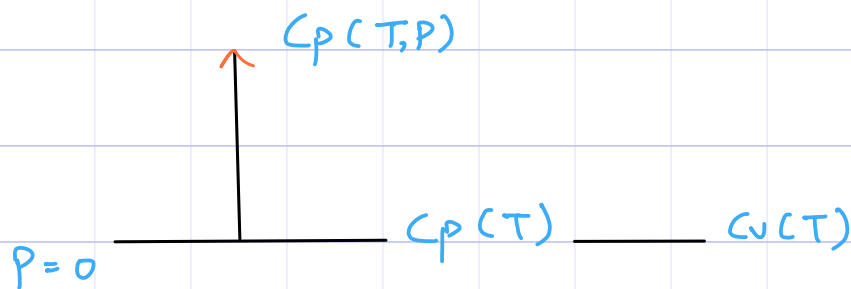
Isothermal Compressibility (α)

Defined as change in volume with respect to change in pressure keeping temperature constant.

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

$\Rightarrow C_p, C_v = f(T)$ at zero pressure

$\rightarrow C_{p0}, C_{v0}$ $P \downarrow, V \uparrow$



$$P \uparrow \left(\frac{\partial C_v}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V$$

$$\left(\frac{\partial C_p}{\partial P} \right)_T = \left(\frac{\partial^2 V}{\partial T^2} \right)_P$$

$$dS = \frac{C_v}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV$$

$$dS = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP$$

Equating the above 2 eqⁿ and solve for 'dT'

$$dT = \frac{T (\partial P / \partial T)_V dV}{C_p - C_v} + \frac{T (\partial V / \partial T)_P dP}{C_p - C_v} \quad \text{--- (A)}$$

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

$$dT = \left(\frac{\partial T}{\partial v} \right)_P dv + \left(\frac{\partial T}{\partial P} \right)_v dP \quad - \textcircled{B}$$

$$(C_p - C_v) = T \left(\frac{\partial v}{\partial T} \right)_P \left(\frac{\partial P}{\partial T} \right)_v \quad - \textcircled{C}$$

Also,

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

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

Replace $\left(\frac{\partial P}{\partial T} \right)_v$ in eqⁿ $\textcircled{C}$

$$C_p - C_v = -T \left(\frac{\partial v}{\partial T} \right)_P^2 \left(\frac{\partial P}{\partial v} \right)_T \quad - \textcircled{D}$$

Now, Isothermal Compressibility $\alpha = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$
Volume Expansivity $\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P$

$$C_p - C_v = -T \underbrace{\left(\frac{\partial v}{\partial T} \right)_P^2}_{\beta^2 v^2} \underbrace{\left(\frac{\partial P}{\partial v} \right)_T}_{-\frac{1}{\alpha v}}$$

$$C_p - C_v = \frac{T \beta^2 v^2}{\alpha v} = \frac{T \beta^2 v}{\alpha}$$

Mayer Relations

Conclusions Drawn from Relation

- ① Isothermal Compressibility is always positive for all substances in all phases, volume expansivity could be negative for some substances but its square is always positive.

Temperature T is thermodynamic temperature ^{which} is also positive, therefore it is concluded that the RHS is always positive or zero $\Rightarrow$ $C_p \geq C_v$

- ② The diff b/w C_p and C_v approaches zero when absolute temperature approaches zero.

665 666, 667

Solved
example

Claypeyson - Clauscius Equation

This equation enables us to determine the change of enthalpy or entropy during a phase change process on the basis of temperature, pressure and specific volume data.

Given the Maxwell Relation $\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial S}{\partial V}\right)_T$

During a phase change process both temperature and pressure remains constant but volume and entropy changes.

$$\left(\frac{\partial P}{\partial T}\right)_{\text{sat}} = \left(\frac{\partial S}{\partial V}\right) = \frac{S_g - S_f}{V_g - V_f} = \frac{S_{fg}}{V_{fg}}$$

$$\boxed{\frac{dP_{\text{sat}}}{dT} = \frac{S_{fg}}{V_{fg}}} \quad \text{Clapeyron Equation} \quad - \textcircled{1}$$

$$dh = Tds + vdp \quad \text{---} \quad \textcircled{2}$$

During Phase change
Press remains constant.

$$dh = Tds$$

So, $\textcircled{1}$ becomes

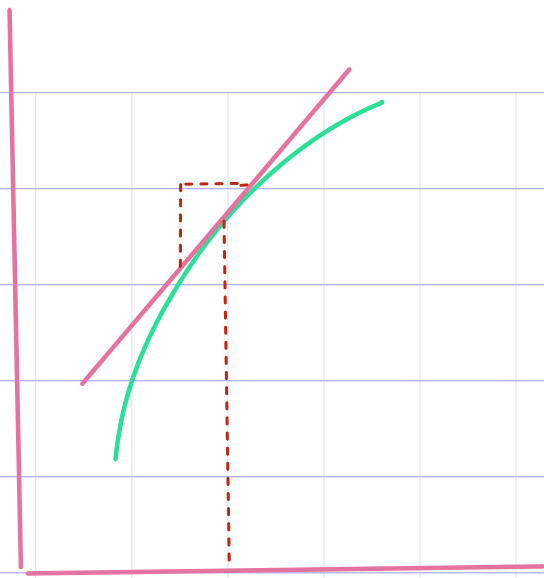
Clapeyron
Eqⁿ $\rightarrow$

$$\boxed{\frac{dP_{\text{sat}}}{dT} = \frac{h_{fg}}{TV_{fg}} = \frac{S_{fg}}{V_{fg}}}$$

$$h_{fg} = TS_{fg}$$

$$\boxed{S_{fg} = \frac{h_{fg}}{T}}$$

This is an important Thermodynamic Relation which enables enthalpy of vapourisation at a given temperature by simply measuring the slope of the curve on a P-T diagram and information about V_f and V_g at that temperature.



① At very low pressure
 $v_g \gg v_f$

$$\frac{dP}{dT} = \frac{h_{fg}}{T v_g}$$

also at low pressure vapour
 phase can be treated like an ideal
 Gas.

$$P v_g = RT$$

$$v_g = \frac{RT}{P}$$

$$\frac{dP_{sat}}{dT} = \frac{P h_{fg}}{RT^2}$$

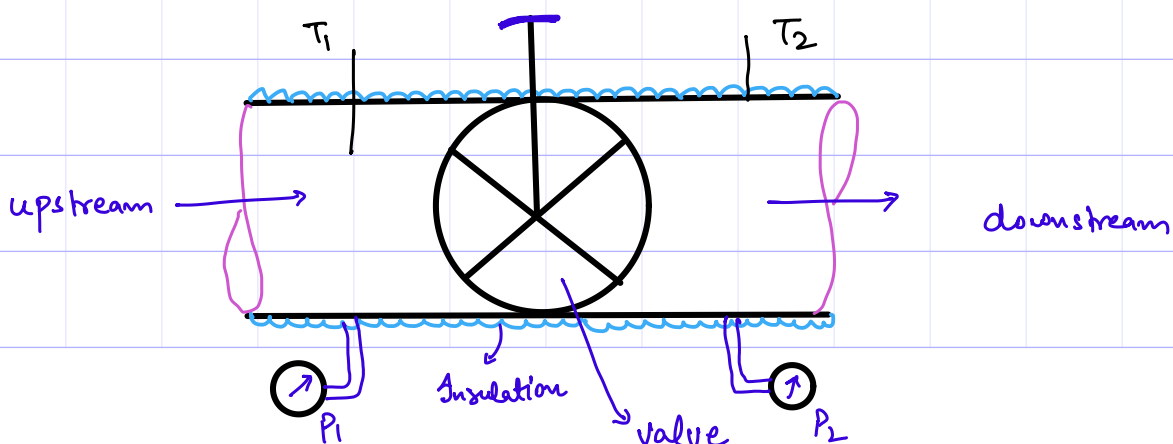
Claypeyron
 Clausius
 Equation

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

$$\ln \frac{P_2}{P_1} = \frac{h_{fg}}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

This equation can be used to determine the variation of
 saturation pressure with temperature. This can also be used
 in solid-vapour region by using the enthalpy of sublimation.

Joule - Kelvin Expansion



Throttling ($\Delta h = 0$)

Throttles are restriction devices which cause significant pressure drop in the fluid. Examples are valves, capillary tube and porous plugs. There is no work done involve during throttling. The pressure drop is mostly accompanied by the large drop in temperature. This is the reason these devices find most $\downarrow$ in refrigeration and air conditioning system.
applications

The magnitude of the pressure drop is governed by the property called Joule-Thompson coefficient. (μ_J)

$$W = 0, Q = 0, h_2 = h_1$$

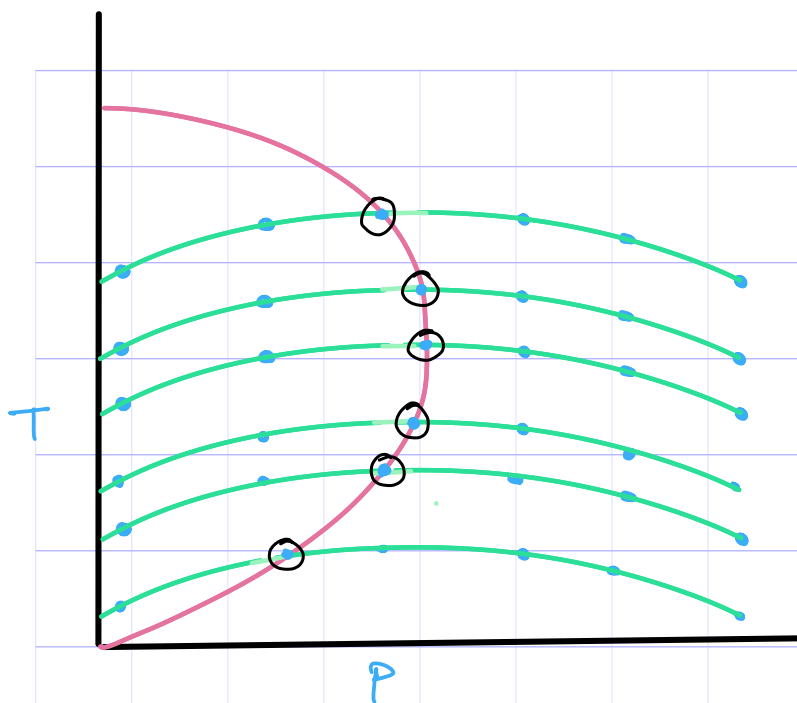
KE, PE

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

Let a real gas pass through a fully opened valve in an insulated pipe having initial pressure and temperature T_1 and T_2 respectively. The valve is closed gradually and pressure and temperature after the valve are noted, keeping P_1 and T_1 at the same value. The valve is closed further and temperature T_2 and P_2 are recorded.

There by getting several readings of P_2 and T_2 .

All the points of diff pressure and temperature after expansion are joined then we obtain a curve on PT plot which is called an isenthalpic process.



Joining the maximas of isenthalpic curve creates an inversion curve.

The numerical value of the slope of the isenthalpic curve on a PT diagram at any point is the Joule-Thomson Coefficient. Inversion curve is obtained by joining all the points where $\mu_J = 0$

When initial temperature and pressure before the valve are given a new value and the experiment is repeated then a different isenthalpic curve is obtained.

The locus of all points where $\mu_J = 0$ is called inversion curve.

The region inside the inversion curve where μ_J is greater than 0 is called the cooling region. The region outside the inversion curve is called heating region.

(Throttling Process)

$$dh = C_p dT + \left\{ v - T \left(\frac{dv}{dT} \right)_P \right\} dP$$

$$C_p dT = - \left\{ v - T \left(\frac{dv}{dT} \right)_P \right\} dP$$

$$C_p \frac{dT}{dP} = T \left(\frac{dv}{dT} \right)_P - v$$

$$\text{or } \mu_J = \frac{1}{C_p} \left\{ T \left(\frac{dv}{dT} \right)_P - v \right\}$$

$$\mu_J = \frac{v}{C_p} \left\{ T \beta_P - 1 \right\}$$

— ①

$\beta_P \rightarrow$ Volume expansivity

Ideal Gas Equation

$$PV = RT$$

$$V = RT/P$$

$$\left(\frac{dv}{dT} \right)_P = \frac{R}{P}$$

but $\frac{R}{P}$ also equals to $\frac{v}{T}$

$$\Rightarrow \frac{R}{P} = \frac{v}{T}$$

From eq (1)

$$\mu_J = \frac{1}{C_p} \left\{ T \left(\frac{dv}{dT} \right)_P - v \right\}$$

$$= \frac{1}{C_p} \left\{ \frac{RT}{P} - v \right\} = \frac{1}{C_p} \{ 0 \}$$

$$\mu_J = 0$$

$\therefore$ A refrigerant must be a real gas.

$$C_p - C_v = -T \left(\frac{dv}{dT} \right)_P^2 \left(\frac{\partial P}{\partial v} \right)_T$$

$$PV = RT ; \quad V = \frac{RT}{P}$$

Real Gas Behaviour

↪ P, V, T

Ideal Gas

It is a hypothetical gas which obeys the law

$$\boxed{PV = RT} \text{ at all pressures and temperatures}$$

However real gases do not follow this equation of state with complete accuracy. As pressure tends to zero, temperature goes to infinity the real gases approach ideal gas behaviour.

C_p and C_v for ideal gas do not change with pressure and volume and are f^n of temperature only.

Internal Energy change of Ideal Gas

Joule's law

$$U = f(T)$$

$$U = f(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

$$\boxed{dU = C_v dT}$$

$$\boxed{dH = C_p dT}$$

Entropy change

$$TdS = dU + PdV$$

$$dS = \frac{du}{T} + \frac{P}{T} dv$$

$$= C_v \frac{dT}{T} + \frac{R}{v} dv$$

$$S_2 - S_1 = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right)$$

$$\Rightarrow Tds = dh - vdp$$

$$ds = \frac{dh}{T} - \frac{v}{T} dp$$

$$ds = C_p \frac{dT}{T} - \frac{R}{P} dP$$

$$S_2 - S_1 = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right)$$

$$\Rightarrow (C_p - C_v) = R$$

$$h = U + PV$$

$$h = U + RT$$

$$dh = dU + RdT$$

$$dh = C_v dT + RdT$$

$$C_p dT = (C_v + R) dT$$

$$C_p - C_v = R$$

- Real Gas z^n
- Compressibility factor

Vander walls Equation

There are 2 assumptions

- ① There a little or no interaction among the molecules of the Gas.
- ② The volume occupied by the molecules themselves is negligibly small compared to total volume of the Gas.

When pressure is small and temperature is very high the internal molecular attraction and the volume of the molecules compare to total volume becomes insignificant and the real gas obey Ideal Gas equation. As the pressure increases the forces of attraction and repulsion becomes significant and the ideal Gas equation is not valid anymore.

Deviation from Ideal Gas behaviour as given by Vanderwall equation of State :

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

Constant 'a' was introduced to account for the existence^{of} mutual attraction among the molecules. $\frac{a}{r^2}$ is called force of attraction.

Constant 'b' was introduced to account for the volume of molecules and is known as co-volume.

Real Gases^{follow} more closely the vander wall equation of state than ideal Gas.

Berthelot Eqⁿ

a, b

$$P = \frac{RT}{V-b} - \frac{a}{TV^2}$$

Compressibility Factor (Z)

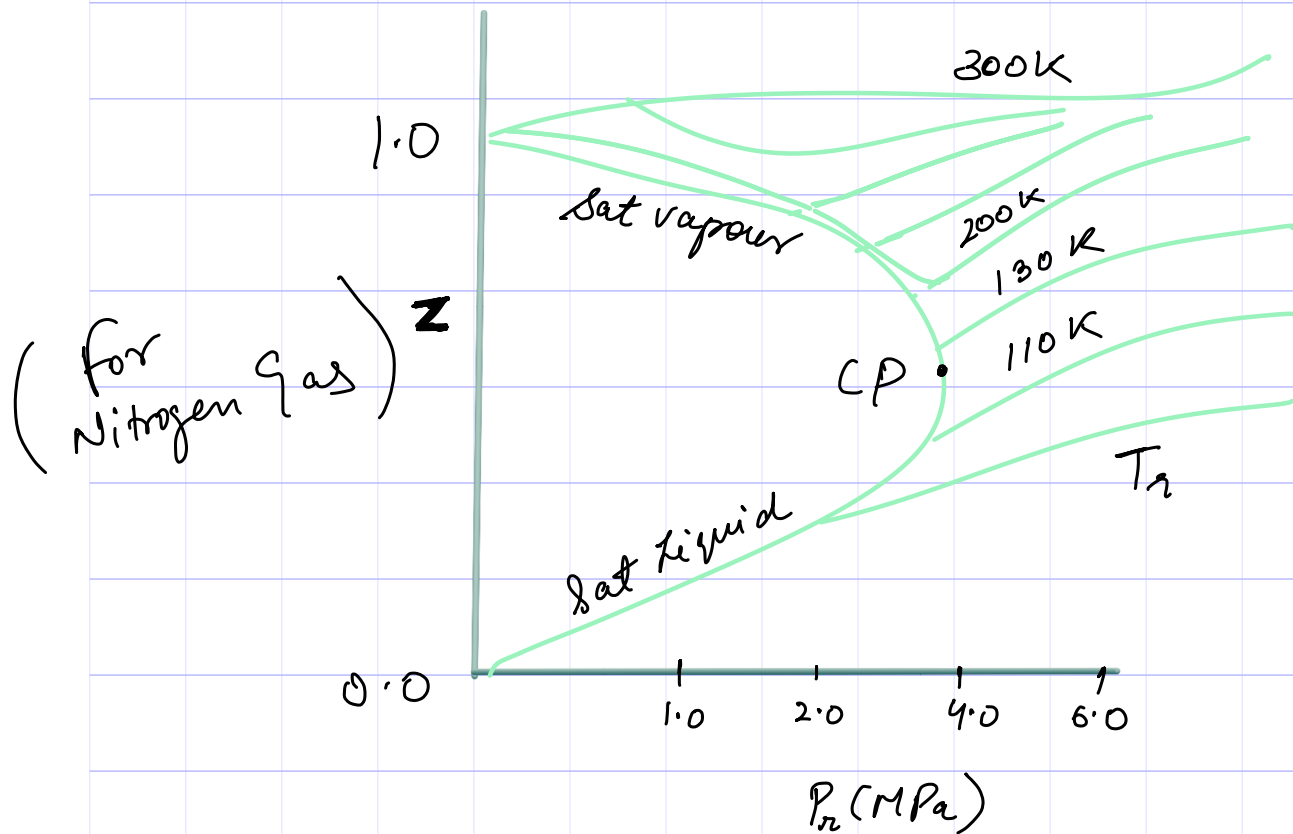
$$Z = \frac{PV}{RT}$$

Compressibility Factor is a quantitative analysis for ideal gas approximately is defined as $Z = \frac{PV}{RT} = 1$ for ideal gas and

the deviation of Z from unity is a measure of deviation of actual behaviour from ideal gas equation of state.

Generalized Compressibility Chart

$$\lim_{P \rightarrow 0} Z = 1$$



Compressibility for N_2 gas is shown following Observations :

- (i) At all temperatures Z approaches 1 as pressure approaches zero, which means as the pressure approaches zero the PV behaviour closely approaches the ideal gas behaviour.

(ii) At room temp above 300K and above Z is near unity upto a pressure of about 10 MPa meaning that the ideal gas eqⁿ of state can be used for N_2 and air in this range with considerable accuracy.

(iii) At const temp on ^{very.} high pressure Z deviates more significantly from the ideal gas value.

Compressibility diagrams for other pure substances show a similar qualitative behaviour.

However quantitatively they will have different values due to different critical temperature and pressure.

In order to put compressibility chart for all substances on a common basis, we reduce the properties with respect to the critical point values.

Reduced Co-ordinates

$$P_r = \frac{P}{P_c} \quad ; \quad T_r = \frac{T}{T_c}$$

If lines of constant T_r are plotted on Z v/s P_r

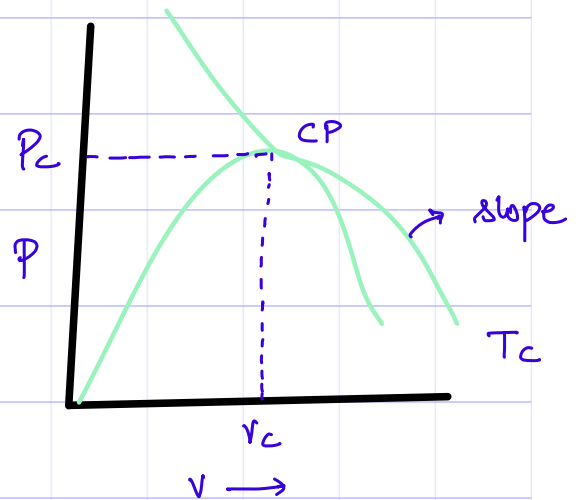
diagram. A Plot is obtained, the more important fact is that these plots are prepared for a number of substances all of them are nearly coincide

Generalized Compression Chart

$$T_c \quad P_c \quad v_r$$

$$v_r = \frac{v}{v_c} = \frac{v}{\frac{RT_c}{P_c}}$$

$$\Rightarrow \left(P + \frac{a}{v^2} \right) (v - b) = RT \quad - (1)$$



$$\left(\frac{\partial P}{\partial v} \right)_{T=T_c} = 0$$

$$\left(\frac{\partial^2 P}{\partial v^2} \right)_{T=T_c} = 0$$

$$T \rightarrow T_c$$

$$v \rightarrow v_c$$

$$P \rightarrow P_c$$

$$v_c = 3b$$

$$T_c = \frac{8a}{27Rb}$$

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

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

$$P_c = \frac{a}{27b^2}$$

$$\left. \begin{aligned} P &= P_r P_c \\ T &= T_r T_c \\ v &= v_r v_c \end{aligned} \right\} - (2)$$

$$\left(P_r P_c + \frac{a}{V_r^2 V_c^2} \right) (V_r V_c - b) = R T_r T_c$$

$$\left(\frac{a}{27b^2} P_r + \frac{a}{9b^2 V_r^2} \right) (3bV_r - b) = R T_r \frac{\partial R}{\partial T_r}$$

$$\left(P_r + \frac{3}{V_r^2} \right) (3V_r - 1) = 8 T_r$$

Vanderwall Equation in Reduced Form

In this equation the constants a and b are omitted also the gas constant is eliminated. This equation is used for many substances.

Law Of Corresponding State

It says that two substances can be said in the corresponding states when their pressure, temperature and volume are fraction of critical pressure, temperature and volume (P_c, V_c, T_c).

$$Pr_a = \frac{P_a}{P_{c,a}}$$

$$= 2$$

$$Pr_b = \frac{P_b}{P_{c,b}}$$

$$= 2, 4, 6$$

Q- Calculate specific volume of Propane at 7 MPa and 150 °C. Using Compressibility factor. Compare the result with specific volume given by ideal Gas equation.

⇒

$$\text{Mol wt} = 44.097 \text{ kg/kmol}$$

$$P_c = 4.26 \text{ MPa}$$

$$T_c = 370 \text{ K}$$

$$Pr = \frac{P}{P_c} = \frac{7}{4.26} = 1.64$$

$$Tr = \frac{T}{T_c} = \frac{423}{370} = 1.143$$

from Compressibility chart, $Z = 0.54$

$$V = \frac{ZRT}{P}$$

$$= \frac{0.54 \times \left(\frac{8.314}{44.097} \right) (423)}{7 \times 10^3}$$

Using Ideal Gas Equation

$$= \underline{6.15 \times 10^{-3} \text{ m}^3/\text{kg}}$$

$$V = \frac{RT}{P}$$

$$= \frac{0.18055 \times 423}{7 \times 10^3}$$

$$= 1.14 \times 10^{-2} \text{ m}^3/\text{kg}$$

Generalized Enthalpy Charts

Also called as Enthalpy Departure.

Development of

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

$$dh = \left(\frac{\partial h}{\partial T} \right) dT + \left(\frac{\partial h}{\partial P} \right) dP \quad \text{--- ①}$$

$$Tds = dh - v dP$$

Divide by dP keep T constant.

$$T \left(\frac{ds}{dP} \right)_T = \left(\frac{\partial h}{\partial P} \right)_T - v$$

$$\left(\frac{\partial h}{\partial P} \right)_T = v + T \left(\frac{ds}{dP} \right)_T$$

$$\left(\frac{\partial h}{\partial P} \right)_T = v - T \left(\frac{\partial v}{\partial T} \right)_P \quad [\text{Maxwell Relation}]$$

Substitute in ①

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left\{ v - T \left(\frac{\partial v}{\partial T} \right)_P \right\} dP \quad \text{--- ②}$$

Isothermal Process

$$\partial h_T = \left\{ v - T \left(\frac{\partial v}{\partial T} \right)_P \right\} dP_T$$

for real Gas $PV = ZRT$

$$V = \frac{ZRT}{P} \quad \& \circ, \quad \left(\frac{\partial V}{\partial T} \right)_P = \frac{ZR}{P} + \frac{RT}{P} \left(\frac{\partial Z}{\partial T} \right)_P$$

Substitute in (2)

$$dh_T = \left\{ \cancel{V} - T \left\{ \frac{\cancel{ZR}}{P} + \frac{RT}{P} \left(\frac{\partial Z}{\partial T} \right)_P \right\} \right\} dP_T$$

$$dh_T = -\frac{RT^2}{P} \left(\frac{\partial Z}{\partial T} \right)_P dP_T$$

$$\begin{cases} P = P_r P_c & \Rightarrow dP = P_c dP_r \\ T = T_r T_c & \Rightarrow dT = T_c dT_r \end{cases}$$

$$dh_{Tr} = -\frac{RT_r^2 T_c^2}{P_r P_c} \left(\frac{\partial Z}{\partial T_c} \right)_{P_r} P_c dP_r T_r$$

$$dh_{Tr} = -RT_r^2 T_c \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r}$$

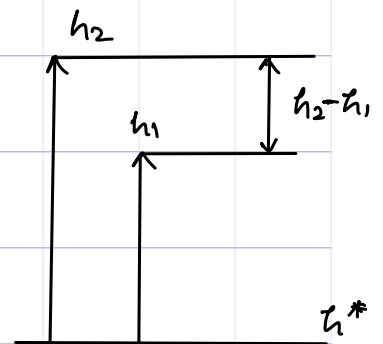
$$\int_1^2 \frac{dh_{Tr}}{T_c} = -R \int_1^2 T_r^2 \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} d(\ln P_r)$$

$$\frac{h_2 - h_1}{T_c} = -R \int_1^2 T_r^2 \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} d(\ln P_r)$$

The RHS of this equation can be obtained by graphical interpretation of the compressibility charts and is a function of T_r and P_r .

The LHS represents enthalpy change.

$$\frac{h^* - h}{RT_c} = T_r^2 \int_0^{P_r} \left(\frac{\partial z}{\partial T_r} \right)_{P_r} d(\ln P_r)$$



This equation is basis for Departure Enthalpy Chart

LHS can be read from Generalized Chart.

The LHS of the equation represents enthalpy change as pressure is increased from 0 to given pressure when temperature is held constant, this quantity is also called Enthalpy Departure.

Use above equation for state ① and ②.

$$\bar{h}_2 - \bar{h} = \bar{R}T_c \left\{ \underbrace{\left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_{T_1, P_1}}_{\text{①}} - \underbrace{\left(\frac{\bar{h}^* - \bar{h}}{\bar{R}T_c} \right)_{T_2, P_2}}_{\text{②}} \right\} + \underbrace{h_{T_2, P_2}^* - h_{T_1, P_1}^*}_{\text{①}}$$

Entropy Chart

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

$$\bar{S}_2 - \bar{S}_1 = \underbrace{(S_2^* - S_1^*)}_{(1)} - R \left\{ \underbrace{\left(\frac{\bar{S}^* - S}{R} \right)_2 - \left(\frac{\bar{S}^* - S}{R} \right)_1}_{(2)} \right\}$$

Internal Energy

ΔU for real gas

$$\bar{h} = \bar{u} + P\bar{v} = \bar{u} + zRT$$

$$(\bar{u}_2 - \bar{u}_1) = (\bar{h}_2 - \bar{h}_1) - R_u (z_2 T_2 - z_1 T_1)$$

Unit - 2

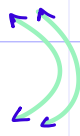
(Mixture of Ideal Gases)

- Concentration

- Mole fraction

- Mass fraction

- Mol. wt.



partial molar Internal Energy

$$U_{mix} = U_A + U_B + \dots$$

In the mixture of ideal gases, each component is uninfluenced by the presence of other components. Each component will be treated as ideal gas. Maintaining the table for each mixture is not possible. Then we try to determine the thermodynamic properties of the mixture from the properties of pure components. Some common mixtures like Air have a well defined table.

Dalton's Model

$$P = P_A + P_B + P_C$$

are partial pressure

$$PV = nRT$$

$$P_A V = n_A RT$$

$$P_B V = n_B RT$$

$$n = PV/RT$$

$$n_A = P_A V/RT$$

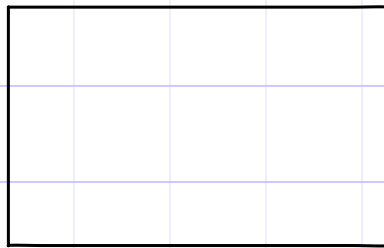
$$n_B = P_B V/RT$$

$$n = n_A + n_B$$

$$\frac{PV}{RT} = \frac{P_A V}{RT} + \frac{P_B V}{RT}$$

$$P = P_A + P_B$$

In the Dalton's Model, each component of the mixture is considered as if the component exists separately and independently at the temperature and volume of the mixture.



Pressure exerted by the component, if the component existing alone at the mixture temperature and volume

$$P_A = y_A P$$

$$P_B = y_B P$$

Amagot Model

In this model the properties of each element are considered as if component exists separately as the pressure and temperature of mixture

Some of the partial volume is 1.