Module- 5

What is thermodynamic relations?

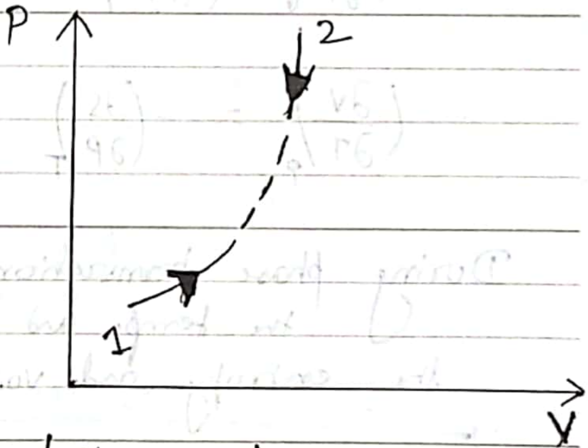
→ Thermodynamic relation refer to the famous maxwell relations which apply for a pure substance undergoing an infinitesimal reversible process defined by four eq^{n}s.

$$dU = Tds - PdV$$

$$dH = Tds + VdP$$

$$dF = -PdV - SdT$$

$$dG = VdP - SdT$$



(U, H, F, G)

These eq^{n}s' apply to the four thermodynamic property and are exact differential of the type,

$$dZ = Mdx + Ndy$$

which can be represented as

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

Using this method on the four equation, we get the maxwell eqn:

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

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

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

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

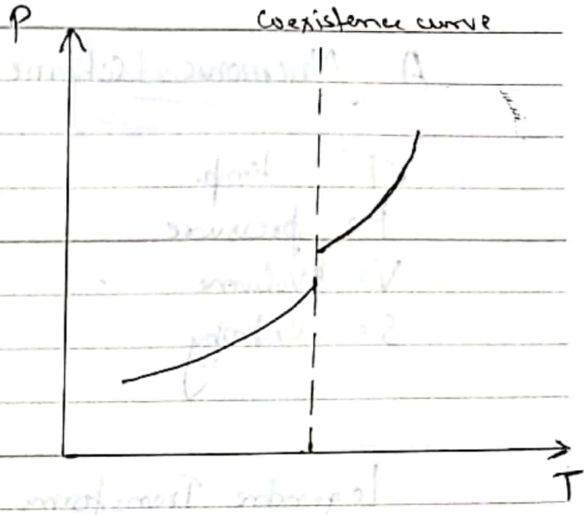
During phase transaction like melting, vapourisation, sublimatio the temp. and pressure remain constant, while the entropy and volume change.

Clausius - Clayperon Relation

This relation helps in differentiating a discontinuous phase transition between two phases of matter denoted by a coexistence curve on a pressure temp. diagram.

It does so, by giving the relation b/w the slope of the tangents to this coexistence curve.

$$\boxed{\frac{dP}{dT} = \frac{l}{T\Delta V}}$$



Joule-Thompson Effect

- There is a temp. change in a real gas or liquid when it is forced through a valve or a porous plug while being kept insulated so that no heat is exchanged with the environment. This effect is called the Joule-Thompson effect and is widely exploited in Thermal machines.

Such as Generators, Heat pumps, and, Air Conditioners

(Q) Consider an Ideal gas of volume 'V' at temp. 'T' and pressure 'p'. If the entropy of the gas is 'S', the partial derivative $\left(\frac{\partial P}{\partial S}\right)_V$ is ______.

(GATE 2017)

Helmholtz and Gibbs function

The ~~bell~~ Helmholtz function is denoted by 'F', $F = U - TS$ —(I)

Gibbs func^n^ denoted by 'G', $G = H - TS$ —(II)

for specific values:-

$$f = u - Ts \quad \text{—(III)}$$

$$g = h - Ts \quad \text{—(IV)}$$

from ~~@~~ 1st law of thermodynamics,

$$dU = dQ - dW$$

and, $dQ = Tds$, $dW = PdV$

$$\boxed{dU = Tds - PdV} \quad \text{—(V)}$$

now,

$$H = U + PV$$

$$\Rightarrow dH = dU + PdV + VdP$$

now,

$$dH = Tds - \cancel{PdV} + \cancel{PdV} + VdP$$

$$\Rightarrow \boxed{dH = Tds + VdP} \quad \text{—(VI)}$$

now, diff eq^n ①

$$dF = dU - Tds - sdT$$

$$\Rightarrow dF = \cancel{Tds} - Pdv - \cancel{Tds} - SdT$$

$$\Rightarrow \boxed{dF = -Pdv - SdT} \text{ — VII}$$

now, diff ⑪

$$dG = dH - Tds - SdT$$

$$\Rightarrow dG = \cancel{Tds} + Vdp - \cancel{Tds} - SdT$$

$$\Rightarrow \boxed{dG = Vdp - SdT} \text{ — VIII}$$

Clausius - Clayperon Eqⁿ

It relates the saturation Pressure (P_{sat}), saturation temp (T_{sat}), enthalpy of vaporisation and sp. volume of 2 phases.

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

$$dS = \left(\frac{\partial S}{\partial T}\right)_V \cdot dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

during a phase change ~~temp~~, $dT = 0$

$$\therefore \boxed{dS = \left(\frac{\partial S}{\partial V}\right)_T \cdot dV}$$

now, 3rd maxwell relation

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

now, substituting we get

$$\left(\frac{\partial P}{\partial T}\right)_V dV = dS \quad \Rightarrow \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{dS}{dV}$$

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Now, 2 phases of a pure substance in eqln, the press. and temp. values become independent of sp. volume. hence, we can write,

$$\left(\frac{dP}{dT}\right)_{saturation} = \frac{ds}{dV}$$

now,

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{S_g - S_f}{V_g - V_f} = \frac{S_{fg}}{V_{fg}}$$ (cause we are talking about two phases)

now, we know that,

$dH = Tds$ or $\Delta H = T\Delta S$

similarly

~~hfg~~ $H_n = T \cdot S_n$

hence, $S_{fg} = \frac{h_{fg}}{T}$.

$$\therefore \boxed{\left(\frac{dP}{dT}\right)_{sat} = \frac{h_{fg}}{T \cdot V_{fg}}} \rightarrow \text{Clausius-clayperon eq}^n$$

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A Mnemonic scheme for thermodynamics

T = temp.
P = pressure
V = Volume
S = entropy

U = Int. energy
H = Enthalpy
F = Helmholtz free energy
G = Gibb's free energy

Legendre Transform (defn)

$$F = U - TS$$
$$H = U + PV$$
$$G = H - TS = U + PV - TS = F + PV$$

D.E. for U, F, H, & G

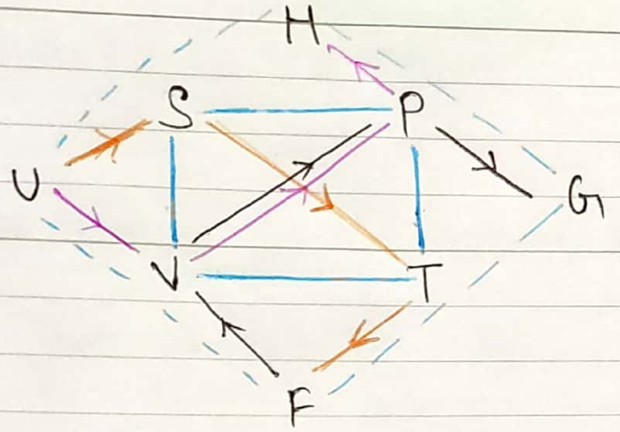
$$dU = TdS - PdV$$
$$dH = TdS + \cancel{PdV}\ VdP$$
$$dF = -SdT - PdV$$
$$dG = -SdT + VdP$$

Maxwell relations

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

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

Trick for Legendre

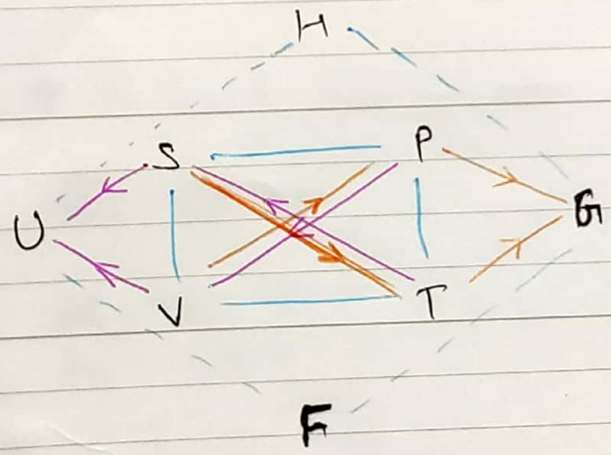


(Satya - prakash
Very - Talented)

$U + PV = H$ | $U - ST = F$

$F + PV = G$ | $H - ST = G$

Trick for D·E



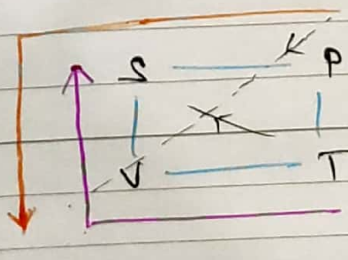
$dU = TdS - PdV$

$dG = VdP - SdT$

$dH = TdS + VdP$

$dF = -PdV - SdT$

Trick for Maxwell



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

for sign (draw arrow from start to end)