3rd SEM
(Paper-6)

LESSON PLAN

Class : 3rd sem Sub : phy(hons) No. of Periods / Weeks :

Sl.No.	Month	Paper/ Unit	Topics assigned	Page No.
1	2	3	4	5
	Decmber	P-6 Unit II	Thermodynamics Variable, Internal energy, Enthalphy, Helmholtz Free energy, Gibbs energy, Thermodynamic potential, Maxwell's Relation using thermodynamics potential Thermodynamics third law Maxwell's thermodynamics relation clausius clapeyron eq^n. Tds eq^n, Energy eq^n	

PROGRESS

PROGRESS

Sl No.	Date	Time	Topics covered (If class not taken, mantion the reasons)	Signature of Teacher
1	2	3	4	5
	2.12.2020	10-11	Introduction for self study	
	4.12	do	- Revision & Discuss about - Thermodynamic variable " Gibbs energy thermodynamics potential.	
	8.12	do	Revision & Discuss Maxwell rel^n, Tds eq^n, energy eq^n	
	10.12	do	- Revision & Discuss . Thermodynamics 3rd law . Clausius eq^n	
	12.12	do	Doubt clearing classes.	

UNIT-II

Thermodynamic variables

The behavior of a thermodynamic system is basically expressed in terms of its macroscopic measurable quantities. The condition of the system at any instant of time is specified by such experimental quantities and we define it as the ***state*** of the system. The set of measurable macroscopic quantities which specify the condition/state of the system at any given instant of time are known as thermodynamic variables. Pressure, volume, temperature etc are examples of such variables. The thermodynamic variables defining the state of a system may be dependent or independent of the mass (or the number of particles). Depending up on their dependence/independence on the mass, the thermodynamic variables are divided into two categories which have been discussed below:

Intensive and extensive variables

If the variables of a thermodynamic system in a given state are independent of the mass or the number of particles of the system, then such variables will be called as ***intensive variables.*** The variables such as pressure for a hydrostatic system, ***surface tension*** for a surface film come under the category of intensive variables. On the other hand, the variables that are dependent on the system's mass or the number of its constituents particles are termed as ***extensive variables.*** Volume in a hydrostatic system, electric dipole moment in a system of dielectric solid etc. are examples of extensive variables. The extensive variables are often expressed in terms of their specific values (*i.e.* the value per unit mass of the system) such as specific volume and the variables obtained so are known as specific variables.
In most of the cases, the mathematical combinations of two intensive variables preserve their nature to be intensive. Suppose x and y are two arbitrary intensive variables then, the combinations xy, x/y, x+y, and will be of intensive kind. However, if X and Y were the arbitrary extensive variables then, the combination X+Y will only be extensive and the rest will work as intensive one. Below is given a table showing the intensive and extensive variables of some of the thermodynamic systems:

The intensive and extensive variables of some thermodynamic Systems

1.	Hydrostatic system	Pressure	Volume
2.	Electric cell	Potential difference	Charge
3.	Dielectric solid	Electric field	Electric dipole moment
4.	Surface film	Surface tension	Area
5.	Paramagnetic substance	Magnetic induction	Magnetic moment
6.	Stretched wire	Tension	Length

Thermodynamic Potentials-

Thermodynamic potentials are scalar quantities used to represent state functions. Together with the corresponding equations of state, thermodynamic potentials describe the equilibrium behavior of a system as a function of so-called "natural variables".

Four common **thermodynamic potentials** are:

(i) Internal energy, U
(ii) Helmholtz free energy, $F = U - TS$
(iii) Enthalpy $H = U + PV$
(iv) Gibbs function $G = U + PV - TS$

Internal Energy

In thermodynamics, **internal energy** (also called the **thermal energy**) is defined as the energy associated with **microscopic forms of energy**. It is an extensive quantity, it depends on the size of the system, or on the amount of substance it contains. The SI unit of **internal energy** is the **joule (J)**. It is the energy contained within the system, excluding the kinetic energy of motion of the system as a whole and the potential energy of the system. **Microscopic forms of energy** include those due to the **rotation**, **vibration, translation**, and **interactions** among the molecules of a substance. None of these forms of energy can be measured or evaluated directly, but techniques have been developed to evaluate the change in the total sum of all these microscopic forms of energy.
In addition, energy is can be stored in the chemical bonds between the atoms that make up the molecules. This energy storage on the atomic level includes energy associated with electron orbital states, nuclear spin, and binding forces in the nucleus.

For an isochoric adiabatic process :
$dU = 0$
$U =$ a constant
the internal energy of system remains constant in an isochoric adiabatic process.

Enthalpy

In thermodynamics, the **enthalpy** is a measurement of energy in a thermodynamic system. It is the thermodynamic quantity equivalent to the total heat content of a system. The **enthalpy** is defined to be the sum of the internal energy **E** plus the product of the pressure **p** and volume **V.** In many thermodynamic analyses the sum of the internal energy U and the product of pressure p and volume V appears, therefore it is convenient to give the combination a name, enthalpy, and a distinct symbol, H.
$H = U + pV$
The enthalpy is the preferred expression of system energy changes in many chemical, biological, and physical measurements **at constant pressure**. It is so useful that it is tabulated in the **steam tables** along with specific volume and specific internal energy. It is due to the fact, it **simplifies the description of energy transfer**. At constant pressure, the enthalpy change equals the energy transferred from the environment through heating **($Q = H_2 - H_1$)** or work other than expansion work. For a variable-pressure process, the difference in enthalpy is not quite as obvious.

For an isobaric adiabatic process :

$dH = 0$
H = a constant
$i.e.$, enthalpy remains constant in a reversible isobaric adiabatic process.

Helmholtz Free Energy

In thermodynamics, the **Helmholtz free energy** is a thermodynamic potential that is defined as the internal energy of the system minus the product of the temperature times the entropy of the system. it measures the "useful" work obtainable from a closed thermodynamic system at a constant volume and pressure.**The Helmhotz free energy** is defined as:

$$F = U - TS.$$

$$dF = -SdT - pdV$$

The internal energy, U, has an exact physical meaning, it is the sum of all the kinetic and potential energies of all the particles in the system. The second term is the amount of spontaneous energy transfer, **TS,** where S is the final entropy of the system. For a constant temperature process the Helmholtz free energy gives all the reversible work. When a physicists say "free energy" without indicating Helmholtz or Gibbs, they usually means Helmholtz free energy, on the other hand, when a chemists say "free energy" they almost always means Gibbs free energy.

For isothermal isochoric process :
$dT = 0$
$dV = 0$
$dF = 0$
F = a constant
$i.e.$ the Helmholtz free energy remains constant during isothermal isochoric process.

Gibbs Free Energy

In thermodynamics, the **Gibbs free energy** is a thermodynamic potential that is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system. Since the **enthalpy** is defined to be the sum of the internal energy **E** plus the product of the pressure **p** and volume **V, the Gibbs free energy** is defined as:

$$G(p,T) = U + pV - TS$$

$$G(p,T) = H - TS$$

The change in **Gibbs free energy, ΔG**, in chemistry, is a very useful parameter. It can be thought of as the maximum amount of work obtainable from a reaction.

For an isobaric and isothermal process :

Hence, if the process is isothermal and isobaric then

$dG = 0$

G = a constant

Thus, Gibbs function (G) or Gibbs free energy remains constant in an isothermalisobaric process.

Significance of Thermodynamic Potential

Since the four function U, F, H and G play in thermodynamics the same role as played by potential energy in mechanics, they are called thermodynamic potentials. Maxwell's thermodynamical relations can be derived from the thermodynamic potentials.

Maxwell's thermodynamical relations are

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

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

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

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

Surface film

It is the thin **film** of liquid near its **surface** and having the thickness equal to the molecular range of attraction for that liquid. The phenomenon of **surface** tension is associated intimately with this **film**

Variation of surface tension with temperature: Eotvos equation The surface tensions of liquids generally decrease with increase of temperature. An empirical relation between surface tension and temperature was developed by Eotvos. According to this relation, if V be the molar volume of a liquid, and Tc the critical temperature of a liquid the surface tension γ is given by $\gamma V^{2/3} = k(T_c - T)$ Where k is constant for all liquids

Thermodynamic Potentials.

The state of a system is described by the variables P, V, T, S, U. But U can be expressed as

$dU = TdS - PdV$

So U can be eliminated. And we have six Pairs as (PV), (PT), (PS), (VT), (VS) & (TS)

But $\delta W = PdV$ & $\delta Q = TdS$

So (P V) & (T S) pair also eliminated and we left only with (PT), (PS), (VT) (VS).

There are four Thermodynamic Potentials.

(i) Internal Energy, U
(ii) Helmholtz free Energy, F
(iii) Enthalpy, H
(iv) Gibbs free Energy, G.

(i) Internal Energy, U.

It is defined as the sum of all kind of energy of a system except its K.E and P.E.

from Ist law

$$dU = \delta Q - \delta W$$

$$\boxed{dU = TdS - PdV}$$

a) for adiabatic

$$dQ = 0$$

$$\boxed{dU = -PdV}$$

b) for Isochoric, adiabatic

$$dV = 0 \quad , \delta Q = 0$$

$$dU = 0$$

$$\boxed{U = \text{constant}}$$

(b) Helmholtz free Energy, F

It is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic System at a constant tempⁿ & volume.

$$F = U - TS$$

we have

$$dU = TdS - PdV$$

$$dF = dU - TdS - SdT$$

$$= \cancel{TdS} - PdV - \cancel{TdS} - SdT$$

$$\boxed{dF = -PdV - SdT}$$

a) Isothermal process

$$dT = 0$$

$$\boxed{dF = -PdV}$$

b) Isothermal Isochoric process

$$dT = 0 \quad , dV = 0$$

$$dF = 0$$

$$\boxed{F = \text{constant}}$$

(c) Enthalpy, H

It is the property of a thermodynamic System. It is equal to the system's internal Energy and the product of its pressure & volume.

At constant pressure change in Entropy is equal to the heat absorbed or released.

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$\boxed{dH = TdS + VdP}$$

a) isobaric

$$dP = 0$$

$$\boxed{dH = TdS}$$

b) Adiabatic Isobaric

$$dH = 0$$

$$\boxed{H = \text{constant}}$$

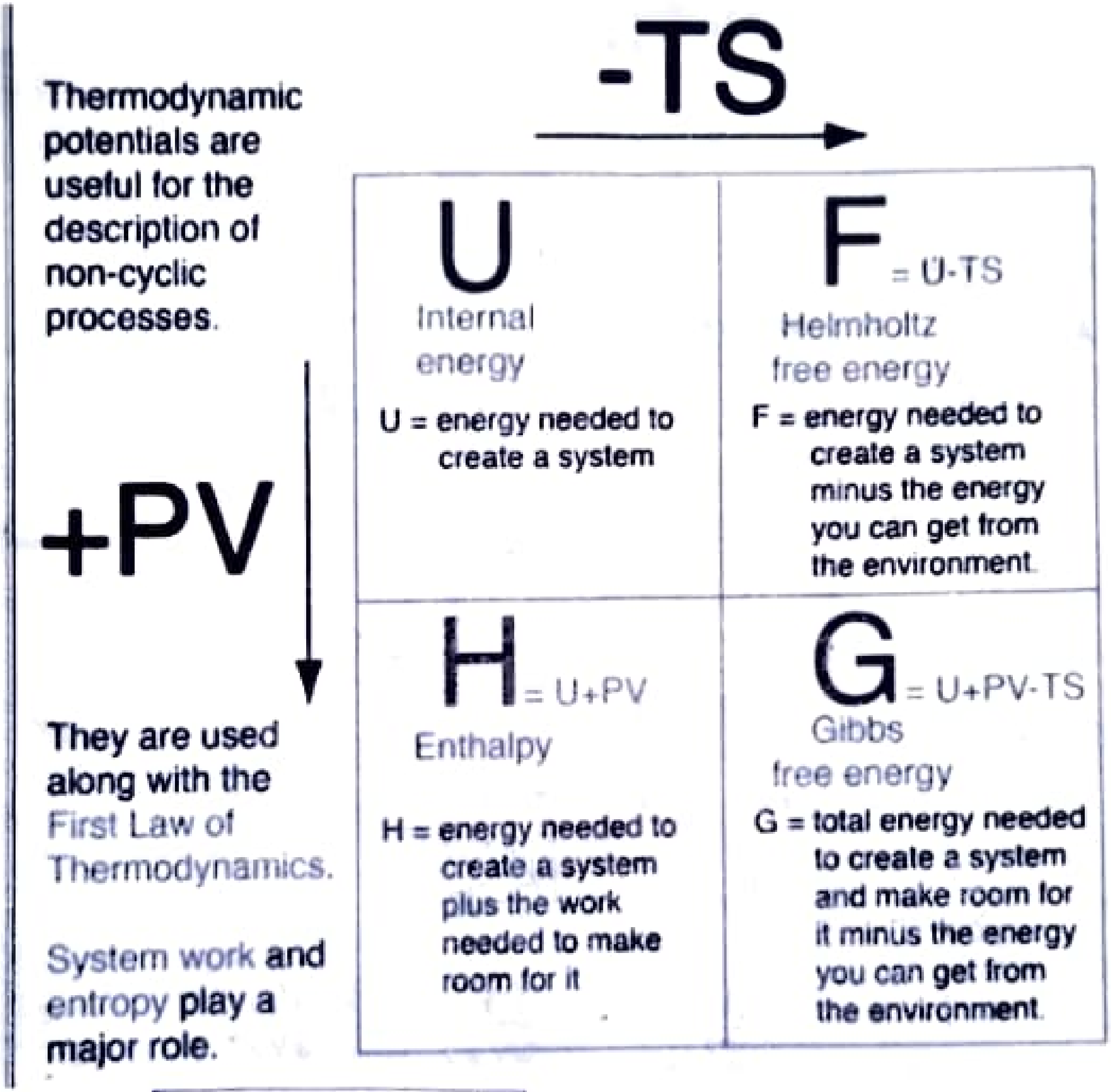
d) Gibbs free Energy, G

It is a thermodynamical potential that can be used to calculate the maximum of reversible work that can be performed by the system at constant Temp & pressure.

$$G = U + PV - TdS$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$



-TS

+PV

Thermodynamic potentials are useful for the description of non-cyclic processes.

They are used along with the First Law of Thermodynamics.

System work and entropy play a major role.

U Internal energy

U = energy needed to create a system

F = U-TS Helmholtz free energy

F = energy needed to create a system minus the energy you can get from the environment.

H = U+PV Enthalpy

H = energy needed to create a system plus the work needed to make room for it

G = U+PV-TS Gibbs free energy

G = total energy needed to create a system and make room for it minus the energy you can get from the environment.

$$\boxed{dG = VdP - SdT}$$

a) iso baric

$$\boxed{dG = -SdT}$$

b) iso baric iso thermal

$$dG = 0$$

$$\boxed{G = \text{constant}}$$

Significance of thermodynamic Potential

The four funⁿ, U, F, H & G plays an important role in thermodynamics as played by the potential energy in mechanics and hence called as thermodynamic potential.

Maxwell's Relation using Thermodynamic Potential.

(i) Internal Energy $U(S,V)$

$$dW = TdS - PdV$$

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

As dW is a perfect diffⁿ

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

Hence

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

(ii) Helmholts funⁿ. $F(T,V)$

$$dF = -PdV - SdT$$

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

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

Hence

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

(iii) Enthalpy, $H(S, P)$

$$dH = TdS + VdP$$

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

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

Hence

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

(iv) Gibbs free Energy, $G(P, T)$

$$dG = VdP - SdT$$

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

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

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

Cooling by Adiabatic Expansion

In an Adiabatic process, the working gas is perfectly insulated from the surroundings so that no heat is allowed to enter or leave. Thus when a highly compressed gas is suddenly allowed to expand adiabatically, it has to perform large amount of external work and an intense cooling results.

Production of low Temp^n

The lowest temp^n corresponds to 0°K (−273.16°C) called the absolute zero temperature.

−65°C can be obtained with the mixture of KOH & ice.

Below −65°C can be achieved by liquefaction of gases.

−268.9°C is reached when lq. He boils under normal pressure.

1 K is achieved when lq. He boils under reduced pressure.

0.4 K can be reached with Liq. He isotope (He^3) boils under reduced pressure.

below 0.4K can be achieved by Adiabatic Demagnetisation.

Adiabatic Demagnetisation

It is a process to acquire a low temp^n by allowing the system to do magnetic work, called Adiabatic Demagnetisation.

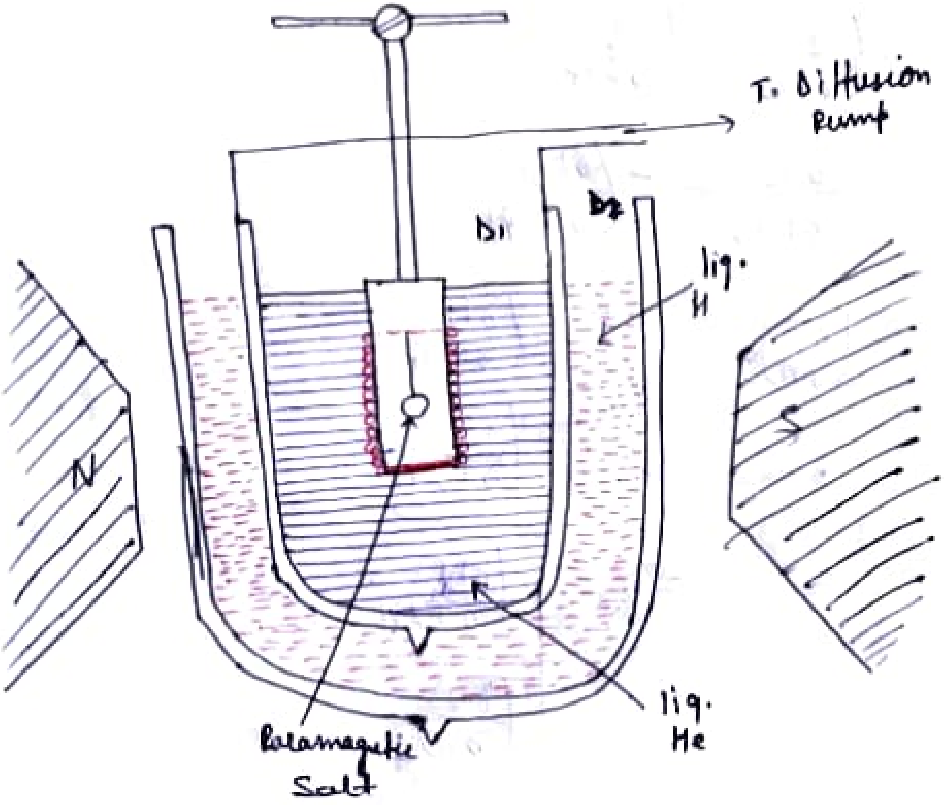
Description :- The paramagnetic salt is suspended in a vessel A surrounded by liq He, which is boiled under reduced pressure. It is surrounded by another Dewar flask D_2 containing liq. H. Mag. field of about 30000 G is applied.

when the mag. field is switched on the salt get magnetised. The heat due to magnetisation is removed with the help of H and pump out, the salt get thermally isolated.

And the salt and liq. He acquire same temp^n. Now magnetic field is switched off/

Then Adiabatic Demagnetisation takes place and temp^n of the specimen ↓es.

The temp^n is measured with a solenoid coil and T can be calculated using curie law.



Theory :- when a paramagnetising salt is placed in a magnetising field H, its elementary dipoles get aligned ‖ to the direction.

The mag. moment per unit volume produced is called Intensity of magnetisation (I).

$$I \propto \frac{H}{T}$$

$$I = C\left(\frac{H}{T}\right)$$

If V is the volume of 1 mole, then intensity of [illegible] salt.

If V is the volume of 1 mole, then intensity of magnetisation of 1 mole of paramagnetic salt.

$$M = IV$$

$$M = CV\left(\frac{H}{T}\right) \Rightarrow \left(\frac{\partial M}{\partial T}\right)_H = \frac{-CVH}{T^2}$$

In terms of thermodynamic system As ↑e in P results in ↓es in V same ↑e in H ↓es the M. Now Replace P by −H and V by M

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

$$\left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_H$$

$$\left(\frac{\partial T}{\partial H}\right)_S = \frac{-T\left(\frac{\partial M}{\partial T}\right)_H}{T\left(\frac{\partial S}{\partial T}\right)_H}$$

$$= \frac{-T\left(\frac{\partial M}{\partial T}\right)_H}{\left(\frac{\partial Q}{\partial T}\right)_H}$$

$$= -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H$$

$C_H \rightarrow$ specific heat at Const. H.

As the process is adiabatic.

$$\boxed{dT = -\frac{T}{C_H}\left(\frac{\partial M}{\partial T}\right)_H dH}$$

so $$\Delta T = -\frac{T}{C_H} \int_{H_1}^{H_2} \left(-\frac{CVH}{T^2} \right) dH$$

$$= +\frac{CV}{C_H T} \int_{H_1}^{H_2} \frac{H}{\cancel{T^2}} \, dH$$

$$\Delta T = \frac{CV}{2 C_H T} \left(H_2^2 - H_1^2 \right)$$

if $H_1 = H$ & $H_2 = 0$

$$\boxed{\Delta T = -\frac{CV}{2 C_H T} H^2}$$

$$\Delta T = \boxed{-\frac{C\,\text{[illegible]}}{C_H T} H^2}$$

Conclusion:-

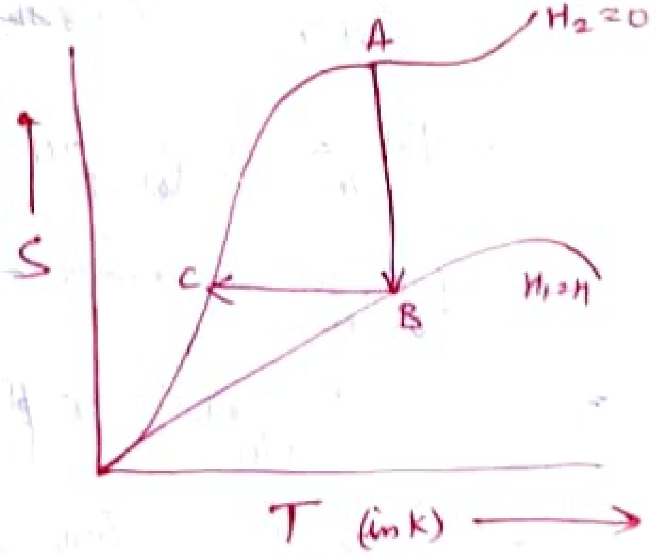
a) the temp^n of a paramagnetic salt decreases on decreasing the magnetic field H.

b) greater is the initial field H, lower is the initial Temp^n T, greater is the temp^n fall ΔT.

(c) CV is called curie constant per mole, if 1 gm of the paramagnetic salt is taken.

T–S Diagram

The cooling produced by adiabatic demagnetisation can be explained using T-S Diagram.



The Entropy of a substance is represented for two values of magnetising field

Magnetic work

we have $\delta Q = dU + PdV$

$$TdS = dU + PdV$$

we know that P is equivalent to Mag. field − H and V is equivalent to Mag. moment M.

$$dU = TdS - PdV$$

$$TdS = dU - HdM$$

$$T\left(\frac{dS}{dM}\right) = \left(\frac{dU}{dM}\right) - H \qquad \{\text{divide by } dM\}$$

using

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \Rightarrow \left(\frac{dS}{dM}\right)_T = -\left(\frac{dH}{dT}\right)_M$$

$$\boxed{-T\left(\frac{dH}{dT}\right)_M = \left(\frac{dU}{dM}\right)_T - H}$$

consider U be a fun^n of T & M

$$U = U(T, M)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{\partial U}{\partial M}\right)_T dM$$

$$TdS = \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{\partial U}{\partial M}\right)_T dM - HdM$$

$$TdS = \left(\frac{\partial U}{\partial T}\right)_M dT + HdM - T\left(\frac{\partial H}{dT}\right)_M dM - HdT$$

$$TdS = \left(\frac{\partial U}{\partial T}\right)_M dT - T\left(\frac{\partial H}{dT}\right)_M dM$$

$$\boxed{TdS = C_M dT - T\left(\frac{dH}{dT}\right)_M dM}$$

Third law of Thermodynamics

This law can be stated in various ways

1. It is impossible to attain the absolute zero by a finite no. of operations. i.e to attain absolute zero an infinite no. of adiabatic / nuclear demagnetisation operation will be needed.

2. The eqm entropies of all systems and the entropy changes in all reversible isothermal processes tend to zero as tempn approaches absolute zero.

As $T \to 0$

$$\lim_{T \to 0} dS \to 0$$

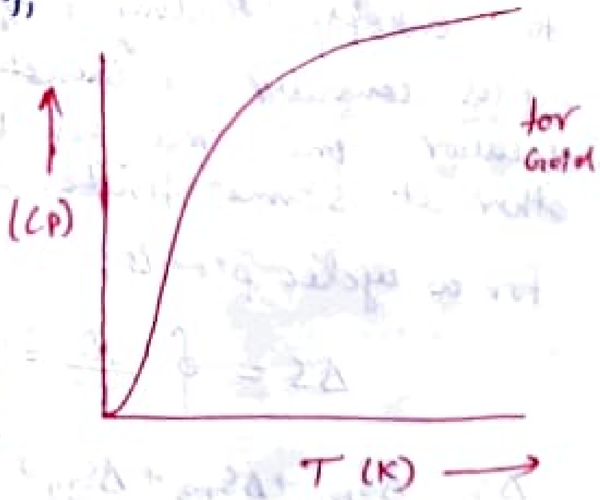
It means that near absolute zero all systems are highly ordered and the entropy of all states is the same

3. within the framework of the first and the second laws we can calculate entropy difference only but with ~~second~~ third law that deals with the entropy at absolute zero.

Consequence of the Third law

1) Heat capacities :→ All Heat capacities must tend to zero as $T \to 0$ K.

we have
$$S(T_2) - S(T_1) = \int_{T_1}^{T_2} C_V \frac{dT}{T}$$



i) when $T_1 \to 0$, acc. to third law integral should be finite and $C_V \to 0$ as $T \to 0$. otherwise the integral will diverge.

ii) Similarly $C_P \to 0$ as $T \to 0$

It was experimentally established by Nernst. It is not compatible with the equipartition of energy. That is third law can't be explained w.r.t classical physics

2) Thermal Expansion stops as $T \to 0$

we have $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ isobaric Expansivity

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

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

if $T \to 0$ then $\alpha \to 0$ (because $S \to 0$ when $T \to 0$ and $\left(\frac{\partial S}{\partial P}\right)_T \to 0$ as $S \to 0$ hence $\alpha \to 0$)

3) No Gas remain Ideal at $T \to 0$

we have, for an ideal gas

$$S = C_V \ln T + R \ln V + C$$

As $T \to 0$, $S \to -\infty$ which has no physical significance or meaning. This means as $T \to 0$ the gas do not behave ideally

Thus third law limits the ideal gas model when temp approach zero.

4. Unattainability of Absolute Zero.

To show that unattainability of absolute zero is eq^n to entropy tending to zero as $T \to 0$.

Let us consider a Carnot engine working b/w two reservoir one maintained at absolute zero and other at some finite temp^n T.

For a cyclic process,

$$\Delta S = \oint \frac{\delta Q}{T} = 0$$

$$\Delta S = \Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41}$$

$$\Delta S_1 = \frac{Q}{T}$$

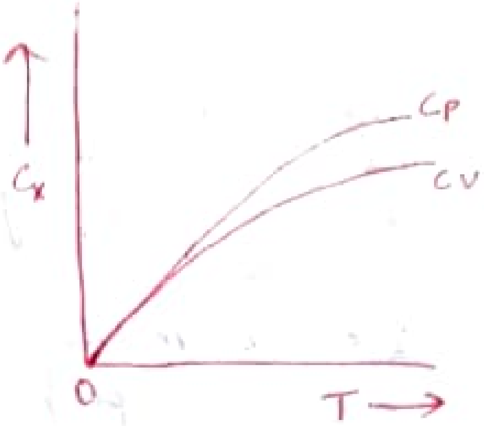
where Q is heat absorbed.

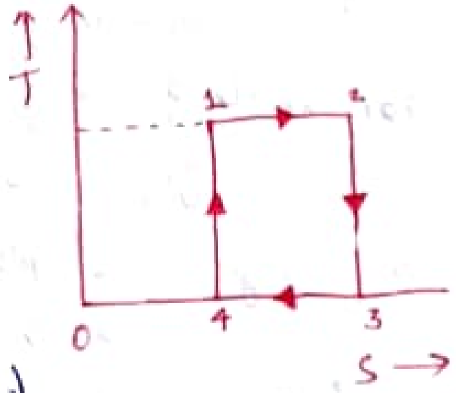
$\Delta S_{23} = \Delta S_{41} = 0$ adiabatic process.

$\Delta S_{34} = 0$ as $T \to 0$ by third law.

Thus,

$$\Delta S = \oint \frac{\delta q}{T} = \Delta S_{12} \neq 0$$





But this contradicts the second law of thermodynamics. Thus we can't operate a carnot engine using a single reservoir i.e it is not possible to attain absolute zero.
(This Expt. is supported by third law).

Phase Transitions

Phase :- A phase of the matter may be defined as a thermodynamic system of which all the physical properties are uniform.

OR

A region of matter that is chemically, physically and mechanically uniform throught called phase.

Phase Transition :- It is a process in which a thermodynamic system changes from one state to another with different physical properties.

Eq^m b/w liq. & Vapours phase.

consider a one component closed system of two phases maintain at constant pressure P and temp^n T. The system consist of a liquid in contact with its vapour.

Let the masses of liq. and vapour phases be m_1 & m_2 and their specific Gibbs Energy be g_1 & g_2.

Thus, $G = m_1 g_1 + m_2 g_2$ At cons. T & P

for small quantity of liquid changes to vapours.

$$\delta G = \delta m_1 g_1 + \delta m_2 g_2$$

As change takes place isothermally & adiabatically so

$$\delta G = 0$$

And $\delta m_1 g_1 + \delta m_2 g_2 = 0$

we have $\delta m_1 = -\delta m_2$

$$\boxed{\text{So } g_1 = g_2}$$

Thus for Eq^n in phase transition the Specific Gibbs & Energies are equal of two phase in one component system.

order of phase Transition

It is defined as the order of the lowest diff^n of the Gibbs function which shows a discontinuity at transition temperature.

First order phase transition

The phase transition which involve latent heat are first order phase transition.

Ex → transition from solid to liquid, liquid to vapours etc. at constant temperature.

The change of phase which takes place at constant temperature and pressure and in which heat is either absorbed or released during change of phase are called first order phase transition.

consider an enclosure containing a liquid and its saturated vapours in Eq^n. If Temp & Pressure remains constant

$$g_1 = g_2$$

Let $T \rightarrow T + dT$

$$g_1 + dg_1 = g_2 + dg_2$$

$$\Rightarrow dg_1 = dg_2$$

from cond^n of saturation

$$\left(\frac{dg_1}{dT}\right)_{sat.} = \left(\frac{dg_2}{dT}\right)_{sat.}$$

when $P \rightarrow P + dP$

$$dg_1 = \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP$$

$$\left(\frac{dg_1}{dT}\right) = \left(\frac{\partial g_1}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)$$

for unit mass

$$dg = VdP - SdT$$

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

$$\left(\frac{\partial g_1}{\partial T}\right)_{sat} = -S_1 + V_1\left(\frac{\partial P}{\partial T}\right)_{sat}.$$

$$\left(\frac{\partial g_2}{\partial T}\right)_{sat} = -S_2 + V_2\left(\frac{\partial P}{\partial T}\right)_{sat}.$$

from Eq^n of Sat^n.

$$S_2 - S_1 = (V_2 - V_1)\left(\frac{\partial P}{\partial T}\right)_{sat}$$

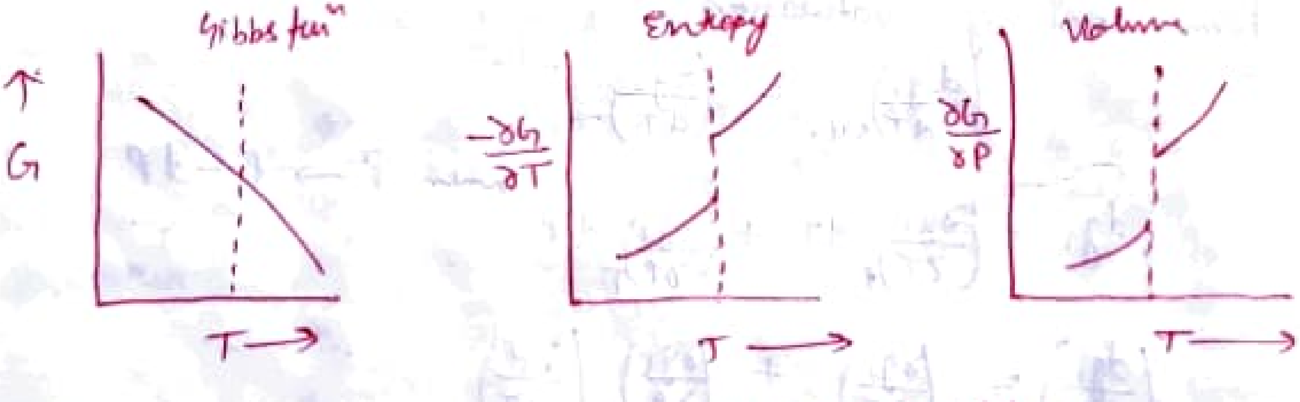
$$\frac{\partial P}{\partial T} = \frac{S_2 - S_1}{V_2 - V_1}$$

$$S_2 - S_1 = \frac{\delta Q}{T} = \frac{L}{T}$$

L → latent heat of vaporization

$$\boxed{\left(\frac{dP}{dT}\right) = \frac{L}{T(V_2 - V_1)}}$$

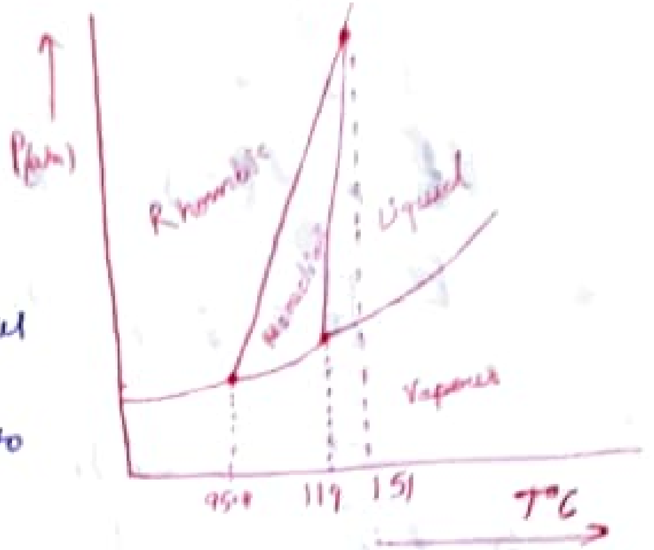
called Clausius Clapeyron latent heat Eq^n.



for Ist order Phase Transition.

The transformation of water into vapours at constant temp^n and volume is first order phase transitions similarly the transformation of ice into water at 0°C and 1 atmospheric pressure is an example of first order phase transition.

Phase diagram of Sulphur



$g_{rh} = g_{mono} = g_{gas}$ at 95.4°C

$g_{mono} = g_{liq} = g_{gas}$ at 119°C

$g_{rh} = g_{mono} = g_{lid}$ at 151°C

At STP stable form of Sulphur is rhombic sulphur.
If heated slowly it changes to solid monoclinic at 95.4 and stable upto 119°C.
If heated further, monoclinic melts and passes into liquid phase.
Thus there are three triple points.

→ During a phase transition, P depends upon T only and is independent of V.

Second order phase Transitions:-

The transition that takes place with no change in entropy and volume at constant temperature and pressure.

Ex→ Transition of liquid helium I to liquid helium II at λ point (2.19 K)
2) Transition of a ferromagnetic material to a paramagnetic material at the curie point.
3. order-disorder transitions in chemical compounds and alloys.

For a phase transition

$$g_1 = g_2$$

$$g_2 - g_1 = 0$$

$$-\left(\frac{\partial g_2}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial T}\right)_P = S_2 - S_1 = 0$$

$$\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T = V_2 - V_1 = 0$$

Also. $$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\frac{C_P}{T} = \left(\frac{\partial S}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\left(-\frac{\partial g}{\partial T}\right)_P\right]_P$$

$$= -\left(\frac{\partial^2 g}{\partial T^2}\right)_P \quad \text{———} \quad (i)$$

Let K be the isothermal compressibility and α is the volume coefficient of expansion.

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

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

$$= -\frac{\partial}{\partial P}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_T$$

$$= -\left(\frac{\partial^2 g}{\partial P^2}\right)_T \quad \text{———} \quad (ii)$$

$$\alpha V = \frac{\partial V}{\partial T}$$

$$\alpha V = \frac{\partial^2 g}{\partial T \partial P} \quad \text{———} \quad (iii)$$

from eq^n ①

$$\frac{C_{P_1}}{T} = -\left(\frac{\partial^2 g_1}{\partial T^2}\right)_P$$

$$\frac{C_{P_2}}{T} = -\left(\frac{\partial^2 g_2}{\partial T^2}\right)_P$$

$$\frac{C_{P_1} - C_{P_2}}{T} = \left(\frac{\partial^2 g_2}{\partial T^2}\right)_P - \left(\frac{\partial^2 g_1}{\partial T^2}\right)_P$$

Similary·

$$V(K_1 - K_2) = \left(\frac{\partial^2 g_2}{\partial P^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial P}\right)_T$$

$$V(\alpha_2 - \alpha_1) = \left(\frac{\partial^2 g_2}{\partial T\,\partial P}\right) - \left(\frac{\partial^2 g_1}{\partial T\,\partial P}\right)$$

from second order Phase Transition eq^n

$$S_2 - S_1 = 0$$

$$S_1 = S_2$$

$$S_1 + dS_1 = S_2 + dS_2$$

$$dS_1 = dS_2$$

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

$$dS = \left(\frac{C_P}{T}\right) dT - \left(\frac{dV}{dT}\right)_P dP$$

$$dS = \left(\frac{C_P}{T}\right) dT - V\alpha\, dP$$

$$dS_1 = \left(\frac{C_{P_1}}{T}\right) dT - V\alpha_1\, dP$$

$$\left(\frac{C_{P_1}}{T}\right) dT - V\alpha_1\, dP = \left(\frac{C_{P_2}}{T}\right) dT - V\alpha_2\, dP$$

$$\boxed{\frac{dP}{dT} = \frac{C_{P_2} - C_{P_1}}{T V(\alpha_2 - \alpha_1)}} \quad (IV)$$

Also,

$$dV_1 = dV_2$$

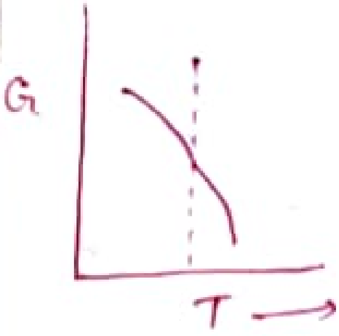
$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

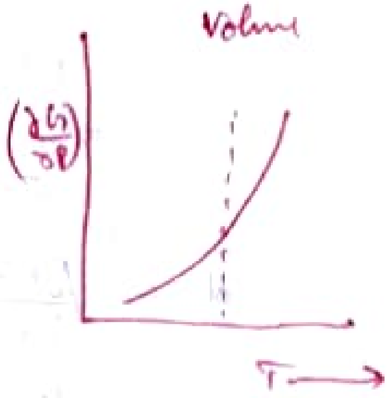
$$dV = V\alpha\, dT - VK\, dP$$

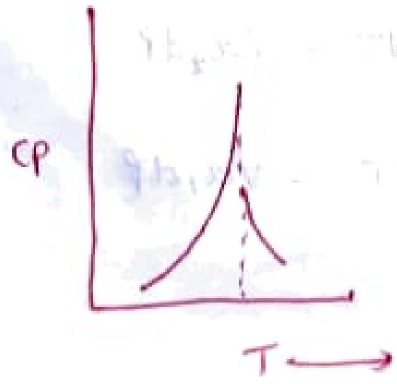
$$V\alpha_1\, dT - VK_1\, dP = V\alpha_2\, dT - VK_2\, dP$$

$$\boxed{\frac{dP}{dT} = \frac{\alpha_2 - \alpha_1}{K_2 - K_1}} \quad (V)$$

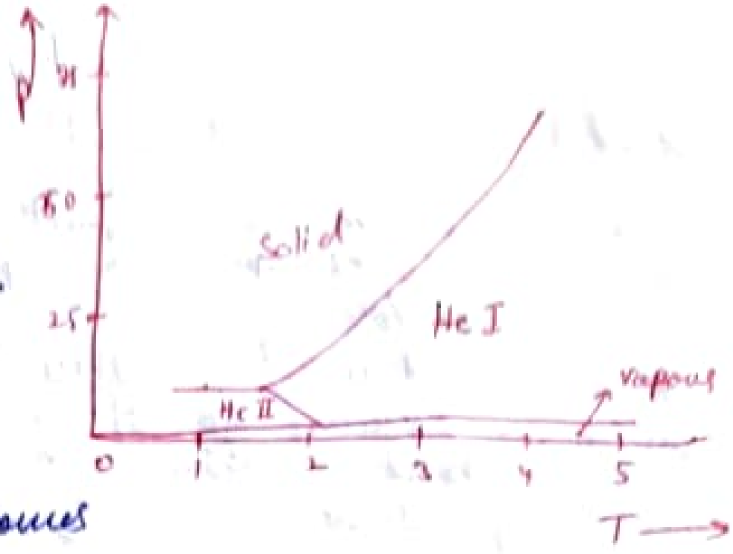
These eqⁿ ④ & ⑤ called as Ehrenfest's eqⁿ.



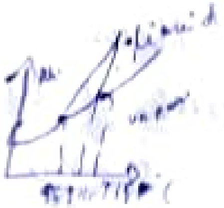




Phase diagram for ⁴He



He has two triple points but no one has the coexistence of solid liquid and vapour phase. because He remains liq. down to absolute zero at atm pressure.
It has extremely weak forces b/w its atoms.



Maxwell's Thermodynamical Relations

Maxwell's Relation

Using the first and Second law of thermodynamics, Maxwell derive six fundamental thermodynamical relations. These equations/Relations have four variables as pressure (P), volume (V), Temperature (T) and entropy (S).

Derivation :- using first law of thermodynamics

$$\delta Q = dU + \delta W \qquad (\delta W = PdV$$

$$\delta Q = dU + PdV$$

$$dU = \delta Q - PdV \qquad \text{—— (i)}$$

using second law,

$$dS = \frac{\delta Q}{T}$$

$$\delta Q = TdS \qquad \text{—— (ii)}$$

from (i) & (ii)

$$dU = TdS - PdV \qquad \text{—— (a)}$$

considering U, S, V to be the funⁿ of two independent variables x & y.

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

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

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

putting these values in Eq^n (a)

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\right]$$

$$- P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy\right]$$

on comparing the coffeient of dx & dy, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \quad \text{——(A)}$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \quad \text{——(B)}$$

Now Diff^n eq^n (A) w.r.t y and (B) w.r.t x

$$\frac{\partial^2 U}{\partial y \partial x} = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y$$

$$+ T\frac{\partial^2 S}{\partial y \partial x} - P\frac{\partial^2 V}{\partial y \partial x}$$

$$\frac{\partial^2 U}{\partial x \partial y} = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x$$

$$- P\frac{\partial^2 V}{\partial x \partial y}$$

The change in internal energy can be brought about by changing V & T.
That's why dU is the perfect differential

$$\therefore \quad \frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}$$

$$\left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x \partial y} =$$

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y \partial x}$$

Since dS and dV are also perfect differentials

Therefore $\dfrac{\partial^2 S}{\partial x \partial y} = \dfrac{\partial^2 S}{\partial y \partial x}$

$$\frac{\partial^2 V}{\partial x \partial y} = \frac{\partial^2 V}{\partial y \partial x}$$

we get

$$\boxed{\left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y}$$

It is the general equation for Maxwell's thermodynamics relations.
In place of x & y we put any two of S, P, T, V
we can have (P, V), (S, T), (S, V), (S, P), (T, V) (T, P)

First Relation

Put $x = S$ and $y = V$

$$\frac{\partial S}{\partial x} = 1 \qquad \frac{\partial V}{\partial x} = 0$$

$$\frac{\partial S}{\partial y} = 0 \qquad \frac{\partial V}{\partial y} = 1$$

using general Equation

$$\left(\frac{\partial T}{\partial y}\right)_x \cdot 1 - \left(\frac{\partial P}{\partial y}\right)_x \cdot 0 = \left(\frac{\partial T}{\partial x}\right)_y \cdot 0 - \left(\frac{\partial P}{\partial x}\right)_y \cdot 1$$

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

Second Relation

Put $x = T$, $y = V$

$$\frac{\partial T}{\partial x} = 1 \qquad \frac{\partial V}{\partial x} = 0$$

$$\frac{\partial T}{\partial y} = 0 \qquad \frac{\partial V}{\partial y} = 1$$

$$0 \cdot \left(\frac{\partial S}{\partial T}\right)_V - \left(\frac{\partial P}{\partial V}\right)_T \cdot 0 = 1 \cdot \left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V \cdot 1$$

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

Third Relation

Put $x = S$ and $y = P$

$$\frac{\partial S}{\partial x} = 1 \qquad \frac{\partial P}{\partial x} = 0$$

$$\frac{\partial S}{\partial y} = 0 \qquad \frac{\partial P}{\partial y} = 1$$

$$\left(\frac{\partial T}{\partial P}\right)_S \cdot 1 - \cancel{\frac{\partial P}{\partial}}\, 1 \cdot \left(\frac{\partial V}{\partial S}\right)_P = 0 - 0$$

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

fourth Relation

Put $x = T$, $y = P$

$$\frac{\partial T}{\partial x} = 1 \qquad \frac{\partial P}{\partial x} = 0$$

$$\frac{\partial T}{\partial y} = 0 \qquad \frac{\partial P}{\partial y} = 1$$

$$0 - 1 \cdot \left(\frac{\partial V}{\partial T}\right)_P = 1 \cdot \left(\frac{\partial S}{\partial P}\right)_T - 0$$

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

Fifth Relation

Put $x = P$ and $y = V$

$$\frac{\partial P}{\partial x} = 1 \qquad \frac{\partial V}{\partial x} = 0$$

$$\frac{\partial P}{\partial y} = 0 \qquad \frac{\partial V}{\partial y} = 1$$

$$\left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V - 0 = \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - 1$$

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

Sixth Relation

Put $x = T$ and $y = S$

$$\frac{\partial T}{\partial x} = 1 \qquad \frac{\partial S}{\partial x} = 0$$

$$\frac{\partial T}{\partial y} = 0 \qquad \frac{\partial S}{\partial y} = 1$$

$$0 - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 - \left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T$$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1}$$

How to Remember Maxwell's Relation's :

Note : The first four Maxwell's thermodynamical relation need not be memorized. These can be easily written by remembering the word *SP* or *T,V,* (sportive). In this, *SP TV* represent entropy, pressure, temperature and volume. In deriving the first two relations, ∂S is written in the numerator on the left hand side of the equation and the rest of the quantities $\partial P, \partial T$ *and* ∂V are written *(i)* in the clockwise order and *(ii)* in the anticlockwise order. In the clockwise direction, the right hand side expression in with a + sign and for the anticlockwise direction, it is –ve. These equations are

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

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

Similarly to write the other equation, ∂S is written in the denominator of the right hand side of the equation and the other quantities are written *(i)* in the anticlockwise direction and *(ii)* in the clockwise direction. These equations are

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

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

Applications of Maxwell's Thermodynamic Relations

1. Specific Heat Equation

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \qquad \delta Q = T\,dS$$

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

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

Now Let S to be a funⁿ of T and V

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

devide by dT

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

multiply by T

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

using Maxwells relation

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

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

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \quad \text{——— (X)}$$

(i) <u>for Ideal Gas</u>

$$PV = RT$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad , \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$C_P - C_V = T\,\frac{R}{V}\,\frac{R}{P}$$

$$= \frac{TRR}{RT} \qquad \{PV = RT$$

$$\boxed{C_P - C_V = R}$$

(ii) <u>for Real Gas</u>

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

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

Diff^n wrt T at constant volume

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

diffⁿ w.r.t T at constant Pressure.

$$0 - \frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = \frac{-RT}{(V-b)^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{R}{(V-b)}$$

$$\left(\frac{\partial V}{\partial T}\right)_P\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right] = \frac{R}{(V-b)}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{\frac{R}{(V-b)}}{\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right]}$$

$$C_P - C_V = \frac{T\frac{R}{(V-b)}\frac{R}{(V-b)}}{\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right]}$$

$$= \frac{\frac{TR}{(V-b)^2}\cdot R}{\left[\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right]}$$

$$= \frac{R}{\left[1 - \frac{2aV^2}{V^3RT}\right]}$$

[neglect b in compⁿ to V]

$$= \frac{R}{\left(1 - \frac{2a}{VRT}\right)}$$

$$= R\left(1 - \frac{2a}{VRT}\right)^{-1}$$

using Binonial, higher power terms can be neglect as a is very small

$$\boxed{C_p - C_v = R\left(1 + \frac{2a}{VRT}\right)}$$

2. To show $C_p - C_v = TE\alpha^2 V$

Let T be the absolute temperature,
E be the isothermal elasticity of the gas
α is the coff^n of volume expansion
V is the specific volume of gas.

from eq^n (X) we have

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \quad \text{—— (ii)}$$

Let P be the fun^n of (V,T)

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

$$\frac{dP}{\cancel{dT}} = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$ [divide by dT

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

at constant pressure $dP = 0$

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

from eq^n (ii), we get

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

Modulus of elasticity E at constant temp^n is given by

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

and cofficient of volume expansion α,

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

we get

$$C_P - C_V = -T(-E)\,\alpha^2$$

$$\boxed{C_P - C_V = +TE\alpha^2 V}$$

we have

$$B_T = \frac{1}{E}$$ where B_T is isothermal compressibility

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

$$\boxed{C_P - C_V = \frac{T\cancel{V}\alpha^2}{B_T}}$$

3. Clausius Clapeyron's Eq^n (First latent Heat Eq^n)

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

Acc. to this whenever there is a change of State the temperature remains constant as long as the change takes place. This Temperature depends upon the pressure and varies from substance to substance.

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

[multiply by T

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

we have $\delta Q = T\,dS$

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

$\left(\frac{\partial Q}{\partial V}\right)_T$ → Shows heat absorbed/rejected per unit change in volume at constant Temp^n.

Let L be the Quantity of heat (Latent heat of substance) require to change the state. And V_2 and V_1 be the specific volume i.e volume per unit mass.

$$\partial Q = L \quad , \quad \partial V = V_2 - V_1$$

$$\frac{L}{(V_2 - V_1)} = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

here dT is the cange in MP/BP due to the change in pressure dP and called latent heat of Eq^n.

Special Case

1) Effect on BP

when liquid → Vapour, volume ↑es, $V_2 > V_1$

T, L are +ve so $\frac{dP}{dT}$ is +ve

Thus BP ↑es with ↑ing the pressure.

(iii) Effect on MP

When a solid melts
Volume ↑es in case of wax type substances
Volume ↓es in case of ice type substance

→ if $V_2 - V_1$ is +ve

$$\frac{dP}{dT} = +ve$$

MP of wax type substance ↑es with ↑e in Pressure.

→ if $V_2 - V_1$ is -ve

$$\frac{dP}{dT} = -ve$$

MP of ice type substance ↓es with ↑e in Pressure.

4. Clausius Second latent heat Eqn.

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$$

where C_2, C_1 are the specific heat of vapours and liquid, L is the latent heat of vapour.

we have,
for change from liquid to vapour

$$S_2 - S_1 = \frac{L}{T}$$

S_1 → entropy of liquid
S_2 → entropy of vapours.

Diffn w.r.t T, we get

$$\frac{dS_2}{dT} - \frac{dS_1}{dT} = \frac{-L}{T^2} + \frac{1}{T}\frac{dL}{dT}$$

Multiply by T

$$T\left(\frac{dS_2}{dT}\right) - T\left(\frac{dS_1}{dT}\right) = \frac{-L}{T} + \frac{dL}{dT}$$

we have $T dS = dQ$

$$\left(\frac{dQ_2}{dT}\right) - \left(\frac{dQ_1}{dT}\right) = \frac{dL}{dT} - \frac{L}{T}$$

$$\boxed{C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}}$$

Clausius second heat eqn.

5. To Prove $E_S/E_T = \gamma = C_P/C_V$

Isothermal Elasticity

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

Adiabatic Elasticity

$$E_S = -V\left(\frac{\partial P}{\partial V}\right)_S$$

$$\frac{E_S}{E_T} = \frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T}$$

Multiply ∂T in Nr & divide ∂S in Dr

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

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

using first four maxwell's Relations,

$$\frac{+\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial S}\right)_V}{\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

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

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

Multiply by T

$(T\,dS = \partial Q)$

$$= \frac{\left(\frac{\partial Q}{\partial T}\right)_P}{\left(\frac{\partial Q}{\partial T}\right)_V} = \frac{C_P}{C_V}$$

$$\boxed{\frac{E_S}{E_T} = \frac{C_P}{C_V} = \gamma}$$

6. Prove that Ratio of Adiabatic to Iso~~thermal~~baric Coffecint of volume expansion,

$$\frac{\alpha_S}{\alpha_P} = \frac{1}{1-\gamma}$$

Adiabatic coff^n of Volume Expansion

$$\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S$$

Isobaric,

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

$$\frac{\alpha_S}{\alpha_P} = \frac{\left(\frac{\partial V}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial T}\right)_P}$$

using Maxwell's Relations :-

$$\frac{ds}{dp} = -\frac{1}{\left(\frac{\partial P}{\partial S}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$$

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

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

we know.

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

$$T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = C_P - C_V$$

$$\frac{ds}{dp} = \frac{-C_V}{C_P - C_V}$$

$$= \frac{1}{1-\left(\frac{C_P}{C_V}\right)}$$

$$\boxed{\frac{ds}{dp} = \frac{1}{1-\gamma}}$$

7. To Prove the ratio of adiabatic to isothermal [illegible] isobaric pressure coefficient of expansion

$$\frac{\beta_S}{\beta_V} = \frac{\gamma}{\gamma-1}$$

we have

$$\beta_S = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_S$$

$$\beta_V = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V$$

$$\beta_S/\beta_V = \frac{\left(\frac{\partial P}{\partial T}\right)_S}{\left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{1}{\left(\frac{\partial T}{\partial P}\right)_S\left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{1}{\left(\frac{\partial V}{\partial S}\right)_P\left(\frac{\partial P}{\partial T}\right)_V} \quad \text{using Relation}$$

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

$$= \frac{T\left(\frac{\partial S}{\partial T}\right)_P \xrightarrow{\quad} C_P}{\underbrace{T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_V}_{C_P - C_V}}$$

$$= \frac{C_P}{C_P - C_V} \quad \text{divide by } C_V$$

$$\boxed{\frac{\beta_S}{\beta_T} = \frac{\gamma}{\gamma-1}}$$

8. To Prove $\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha$

and show that heat is generated when a substance which expands on heating is compressed and for substance which contracts cooling takes places.

we have

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

Multiply by T

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

$T\,dS = dQ$

$$\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P \quad \text{———— (i)}$$

we have $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

$$\left(\frac{\partial V}{\partial T}\right)_P = \alpha V$$

from (i)

$$\boxed{\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha}$$

is the required relation

Case I when α is +ve

Substance expands on heating & $\left(\frac{\partial Q}{\partial P}\right)_T = -ve$

means heat must be releases.

Thus, we can say that Increase in pressure heats a body that expands on rise of Temp^n.

Case II when α is −ve

substance contracts on heating & $\left(\frac{\partial Q}{\partial P}\right)_T = +ve$

means heat is added.

Thus we can say that cooling is produced when a substance, which contracts on heating, suddenly compresses.

9. T·dS Equations

(i) first Tds Eq^n

Let entropy S to be a fun^n of Temp^n and volume only.

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

we get

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

Multiply by T
$TdS = dq$

$$TdS = T\underset{\downarrow C_v}{\left(\frac{\partial S}{\partial T}\right)_v} dT + T\left(\frac{\partial S}{\partial v}\right)_T dv$$

$$\boxed{TdS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv}$$

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

(ii) Second Tds Eq^n

Let Entropy S to be a fun^n of Temp^n & Pressure only.

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

Multiply by T

$$TdS = T\underset{\downarrow C_P}{\left(\frac{\partial S}{\partial T}\right)_P} dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$\boxed{TdS = C_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP}$$

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

(iii) Third TdS Eqⁿ.

Let s to be a fnⁿ of (P, v)

$$ds = \left(\frac{\partial S}{\partial P}\right)_V dP + \left(\frac{\partial S}{\partial V}\right)_P dV$$

Multiply by T

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV$$

$$Tds = T\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P dV$$

$$\boxed{TdS = \cancel{T}\, C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV}$$

10. Energy Equations:-

These Eqn gives an idea of how Internal Energy of a gas varies with volume even when tempⁿ remains constant.

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

①

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

we have

$$dU = \delta Q - \delta W$$

$$dU = TdS - PdV$$

divide by dV

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

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

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

called as First Energy Eqⁿ.

Also

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

Case I for Ideal gas

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

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

we get $$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0}$$

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

Case II for Real gas

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

$$T\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} = P + \frac{a}{V^2}$$

we get $$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}}$$

$$\boxed{dU = C_v\,dT + \frac{a}{V^2}\,dV}$$

② $$U = U(T, P)$$

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

$$dU = TdS - PdV$$

divide by dP

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

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

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

called Second Energy eqn.

$$dU = C_P\,dT - \left[T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial P}\right)_T\right]$$