

Application of Maxwell's relations

I Tds equations

Entropy (S) of a pure substance can be taken as a function of temperature (T) and volume (V).

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \quad \text{--- (1)}$$

Multiplying both sides by T

$$T dS = T \left(\frac{\partial S}{\partial T} \right)_V dT + T \left(\frac{\partial S}{\partial V} \right)_T dV \quad \text{--- (2)}$$

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

and from Maxwell's relations

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

Putting these values in (2)

$$T dS = C_V dT + T \left(\frac{\partial P}{\partial T} \right)_V dV \quad \text{--- (3)}$$

This is called the first Tds equation.

□ The entropy S of a pure substance can also be regarded as a function of temperature (T) and pressure (P)

$$dS = \frac{dq}{T}$$

$$dq = C_v dT$$

$$T ds = C_v dT$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad (4)$$

Multiplying both sides by T

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

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

and from Maxwell's relation

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

Put these values in (4)

$$T ds = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_P dP \quad (5)$$

Equation (5) is called Second Tds equation.

$$dq = C_v dT$$

$$T ds = \frac{dq}{T} = C_v \frac{dT}{T}$$

$$C_v = T \frac{ds}{dT}$$

(2) Deduce ~~clapeyron's~~ Clausius - Clapeyron latent heat equation from Maxwell's thermodynamical relations.

Ans :- From Maxwell's relation

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

Multiplying both sides by T we have

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

From Second law of thermodynamics

$$T \partial S = \partial Q$$

$$\left(\frac{\partial Q}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V \quad \text{--- (1)}$$

Here $\left(\frac{\partial Q}{\partial V} \right)_T$ represent the quantity of heat absorbed per unit change in volume at constant temperature.

This means that at constant temperature the heat absorbed or liberated brings out simply a change in the volume of the substance. Therefore, this quantity of heat absorbed or liberated at constant temperature must be the latent heat and the change in volume must be due to a change of state. If ∂Q be the latent heat (L) when a unit mass of the substance changes in volume from V_1 to V_2 at constant temperature, then

$$\partial Q = L \text{ and } \partial V = V_2 - V_1$$

Putting these values in (1)

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

$$\text{or } \frac{L}{V_2 - V_1} = T \frac{dP}{dT}$$

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

This is the required Clausius - Clapeyron's latent heat equation

(5) show that for a homogeneous fluid

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

where the symbols have their usual meanings.

(a) Hence prove that for a perfect gas

$$C_p - C_v = R$$

(b) Hence prove that for a van der Waal's gas

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

Ans :— The specific heats at constant pressure and at constant volume are given as —

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p \quad [\partial Q = T \partial S]$$

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

Considering entropy (S) as a function of temperature and volume.

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

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

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

From Maxwell's relation

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

$$\therefore \left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial S}{\partial T} \right)_v + \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p$$

Multiplying by T both sides

$$T \left(\frac{\partial S}{\partial T} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_v + T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p$$

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

$$C_p - C_v = T \left(\frac{\partial p}{\partial T} \right)_v \left(\frac{\partial v}{\partial T} \right)_p \quad \text{--- (1)}$$

(a) For a perfect gas

$$pV = RT$$

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

Hence (1) becomes

$$C_p - C_v = T \left(\frac{R}{V}\right) \left(\frac{R}{P}\right) = \frac{R^2 T}{P V}$$

$$C_p - C_v = \frac{R^2 T}{R T} \quad \left| \quad pV = RT \right.$$

$$\boxed{C_p - C_v = R} \quad \text{--- (2)}$$

(b)

For a Vander Waal's gas
the equation of state is

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

where a and b are constants

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

Differentiating w.r.t T at constant volume

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

Differentiating w.r.t T at constant pressure

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

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

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

Substituting these values of $\left(\frac{\partial p}{\partial T}\right)_v$ and $\left(\frac{\partial v}{\partial T}\right)_p$ in equation (1), we have

$$C_p - C_v = T \left(\frac{R}{v-b}\right) \left(\frac{R}{v-b}\right) \frac{1}{\left[\frac{RT}{(v-b)^2} - \frac{2a}{v^3}\right]}$$

$$C_p - C_v = \frac{RT/(v-b)^2 \cdot R}{\frac{RT}{(v-b)^2} \left[1 - \frac{2a(v-b)^2}{v^3 RT}\right]}$$

$$C_p - C_v = \frac{R}{\left(1 - \frac{2a(v-b)^2}{v^3 RT}\right)}$$

Neglecting b as compared to v

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

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

Expanding binomially and neglecting a in higher powers, we have

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

(4) Show that

$$C_p - C_v = TE\alpha^2 v$$

Where C_p, C_v are the specific heats at constant pressure and volume respectively. E the bulk modulus of elasticity, α the coefficient of volume expansion and v the specific volume.

$$\text{Solution} \rightarrow C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p$$

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

Now the entropy S is regarded as a function of T and v and since dS is a perfect differential.

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

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

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

From Maxwell's relation

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

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

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

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p \quad \text{--- (1)}$$

P is a function of T and v and dP is a perfect differential, hence

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

If the change takes place at constant pressure, $dP = 0$, then

$$\left(\frac{\partial p}{\partial T}\right)_V dT = -\left(\frac{\partial p}{\partial V}\right)_T dV$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (2)}$$

Substituting (2) in (1)

$$C_p - C_v = T \left[-\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \right] \left(\frac{\partial V}{\partial T}\right)_P$$

$$= -T \left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 \quad \text{--- (3)}$$

But $E = -\left(\frac{\partial p}{\partial V/V}\right)_T = -V \left(\frac{\partial p}{\partial V}\right)_T$

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

Putting these in (3)

$$C_p - C_v = +T \cdot \frac{E}{V} \cdot \alpha^2 V^2$$

$$C_p - C_v = TE \alpha^2 V \quad \checkmark$$

(5) Using Maxwell's thermodynamical relations prove that for any substance, the ratio of the adiabatic and isothermal elasticities is equal to the ratio of the two specific heats.

Solution \rightarrow The coefficient of volume elasticity is defined as

$$E = \frac{\text{stress}}{\text{volume strain}} = \frac{-dp}{dV/V}$$

$$E = -V \frac{dp}{dV}$$

The adiabatic elasticity E_s (constant volume) and isothermal elasticity E_T (temperature constant) are given by

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

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

Hence
$$\frac{E_s}{E_T} = \frac{\left(\frac{\partial P}{\partial V} \right)_S}{\left(\frac{\partial P}{\partial V} \right)_T}$$

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

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

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

From Maxwell's relations

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

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

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

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

$$\left. \begin{array}{l} T, P, S, V \\ S, V, T, P \\ P, T, V \end{array} \right\}$$

Substituting in (1)

$$\frac{E_s}{E_T} = \frac{-\left(\frac{\partial v}{\partial T}\right)_p \times -\left(\frac{\partial p}{\partial s}\right)_v}{\left(\frac{\partial v}{\partial s}\right)_p \times \left(\frac{\partial p}{\partial T}\right)_v}$$

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

$$\frac{E_s}{E_T} = \frac{T \left(\frac{\partial s}{\partial T}\right)_p}{T \left(\frac{\partial s}{\partial T}\right)_v}$$

$$\boxed{\frac{E_s}{E_T} = \frac{C_p}{C_v} = \gamma} \quad \checkmark$$

⑥ Using Maxwell's thermodynamical relations, Prove that the ratio of the adiabatic to the isobaric coefficient of expansion is $\frac{1}{1-\gamma}$

Proof \rightarrow Adiabatic Volume Coefficient of expansion

$$\alpha_s = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_s ; \text{--- (1)}$$

Isobaric Volume Coefficient of expansion

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p ; \text{--- (2)}$$

$$\therefore \frac{\alpha_s}{\alpha_p} = \frac{\frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_s}{\frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p}$$

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

But from Maxwell's relation

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

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

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

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

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

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

$$\text{and } C_v = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$\frac{ds}{dp} = \frac{C_v}{-(C_p - C_v)}$$

$$\frac{ds}{dp} = \frac{C_v/C_v}{-\left(\frac{C_p}{C_v} - \frac{C_v}{C_v}\right)}$$

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

Proved

(b) Using Maxwell's thermodynamic relations prove that the ratio of the adiabatic to the isochoric pressure coefficient of expansion is equal to $\left(\frac{\gamma}{\gamma-1}\right)$.

Proof \rightarrow Adiabatic pressure coefficient of expansion

$$\beta_s = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_s \quad \text{--- (1)}$$

Isochoric pressure coefficient of expansion

$$\beta_v = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_v \quad \text{--- (2)}$$

$$\frac{\beta_s}{\beta_v} = \frac{\frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_s}{\frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_v}$$

$$\frac{\beta_s}{\beta_v} = \frac{\left(\frac{\partial p}{\partial T} \right)_s}{\left(\frac{\partial p}{\partial T} \right)_v}$$

$$= \frac{1}{\left(\frac{\partial T}{\partial p} \right)_s \left(\frac{\partial p}{\partial T} \right)_v}$$

But From Maxwell's relations

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

$$\frac{\beta_s}{\beta_v} = \frac{1}{\left(\frac{\partial v}{\partial s} \right)_p \left(\frac{\partial p}{\partial T} \right)_v}$$

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

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

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

$$= \frac{C_p}{C_p - C_v}$$

$$\frac{\beta_s}{\beta_v} = \frac{C_p / C_v}{\frac{C_p}{C_v} - \frac{C_v}{C_v}}$$

$$\boxed{\frac{\beta_s}{\beta_v} = \frac{\gamma}{\gamma - 1}} \quad \text{Proved.}$$

⑦ Using Maxwell's thermodynamical relation show that

$$\left(\frac{\partial C_v}{\partial v} \right) = T \left(\frac{\partial^2 s}{\partial v \partial T} \right) = T \left(\frac{\partial^2 p}{\partial T^2} \right)_v$$

Proof → From Maxwell's relations

$$\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v \quad \text{--- (1)}$$

Differentiating (1) w.r.t to T

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

$$\left(\frac{\partial^2 s}{\partial T \partial v} \right) = \left(\frac{\partial^2 p}{\partial T^2} \right)_v \quad \text{--- (2)}$$

$$\text{But } C_v = T \left(\frac{\partial s}{\partial T} \right)_v \quad \text{--- (3)}$$

Differentiating (3) w.r.t v

$$\left(\frac{\partial C_v}{\partial v} \right) = T \left(\frac{\partial^2 s}{\partial T \partial v} \right) \quad \text{--- (4)}$$

From (2) and (4)

$$\left(\frac{\partial C_v}{\partial v}\right) = T \left(\frac{\partial^2 s}{\partial T \partial v}\right) = T \left(\frac{\partial^2 p}{\partial T^2}\right)_v \quad (5)$$

(8) Using Maxwell's thermodynamical relations, show that

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

Proof \rightarrow From Maxwell relation

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

Differentiating (1) w.r.t T

$$\left(\frac{\partial^2 s}{\partial T \partial p}\right) = - \left(\frac{\partial^2 v}{\partial T^2}\right)_p \quad (2)$$

$$\text{But } C_p = T \left(\frac{\partial s}{\partial T}\right)_p \quad (3)$$

Differentiating (3) w.r.t pressure

$$\left(\frac{\partial C_p}{\partial p}\right) = T \left(\frac{\partial^2 s}{\partial T \partial p}\right); \quad (4)$$

From (2) and (4)

$$\left(\frac{\partial C_p}{\partial p}\right) = T \left(\frac{\partial^2 s}{\partial T \partial p}\right) = -T \left(\frac{\partial^2 v}{\partial T^2}\right)_p \quad (5)$$

(9) Show that for a perfect gas

$$\left(\frac{\partial u}{\partial v}\right)_T = 0$$

Proof \rightarrow From Maxwell first relation

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

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

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

But $dQ = dU + PdV$

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

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

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

But from perfect gas equation

$$PV = RT$$

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

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

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

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

$$\left(\frac{\partial U}{\partial V} \right)_T = P - P = 0$$

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad \text{Proved}$$

(10) Prove that

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

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

(P) Proof → Considering the pressure (P) as a function of two independent variables S and T i.e.

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

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

If the process is isobaric i.e. change takes place at constant pressure
 $dP = 0$

$$\left(\frac{\partial P}{\partial S}\right)_T dS + \left(\frac{\partial P}{\partial T}\right)_S dT = 0$$

$$\text{or } \left(\frac{\partial P}{\partial S}\right)_T dS = -\left(\frac{\partial P}{\partial T}\right)_S dT$$

$$\therefore \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_S \quad \text{Proved}$$

(ii) Considering P as a function of T and V
 $P = f(T, V)$

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

In isobaric process, $dP = 0$

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

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

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

Proved

(11) Prove that

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

Proof \rightarrow

From Maxwell's relation

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

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

$$\text{But } T\partial S = \partial Q$$

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

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

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

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