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Maxwell's Thermodynamical Relation

There are four thermodynamical quantities Press P, Volume V, Temp T and entropy (S). The 1st & second Law of thermodynamics are

$$dQ = du + PdV \quad \text{--- (1)}$$

$$\& \quad dQ = TdS \quad \text{--- (2)}$$

$$\therefore \quad \boxed{TdS = du + PdV} \quad \text{--- (3)}$$

Let S, u and V are independ function of two variables x and y

(i) $S = f(x,y)$

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

(ii) $U = f(x,y)$

$$\therefore du = \left(\frac{\partial u}{\partial x}\right)_y dx + \left(\frac{\partial u}{\partial y}\right)_x dy.$$

(ii) $V = f(x,y)$

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

From equ^n (3)

$$T\cdot\left(\frac{\partial S}{\partial x}\right)_y dx + T\left(\frac{\partial S}{\partial y}\right)_x dy = \left(\frac{\partial u}{\partial x}\right)_y dx + \left(\frac{\partial u}{\partial y}\right)_x dy + P\cdot\left(\frac{\partial V}{\partial x}\right)_y dx + P\left(\frac{\partial V}{\partial y}\right)_x dy.$$

Comparing the coefficient of dx & dy.

$$T\left(\frac{\partial S}{\partial x}\right)_y = \left(\frac{\partial u}{\partial x}\right)_y + P\left(\frac{\partial V}{\partial x}\right)_y \quad \text{--- (4)}$$

$$\text{And } T\left(\frac{\partial S}{\partial y}\right)_x = \left(\frac{\partial u}{\partial y}\right)_x + P\left(\frac{\partial V}{\partial y}\right)_x \quad \text{--- (5)}$$

Differentiating equ^n 4 w.r.to y and equ^n 5 with respect x

$$T.\cancel{\frac{\partial^2 S}{\partial x \partial y}} + \left(\frac{\partial S}{\partial x}\right)_y \cdot \left(\frac{\partial T}{\partial y}\right)_x = \cancel{\frac{\partial^2 U}{\partial x \cdot \partial y}} + P.\cancel{\frac{\partial^2 V}{\partial x \partial y}} + \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y \quad -(6)$$

$$\& \ T.\cancel{\frac{\partial^2 S}{\partial x \partial y}} + \left(\frac{\partial S}{\partial y}\right)_x \cdot \left(\frac{\partial T}{\partial x}\right)_y = \cancel{\frac{\partial^2 U}{\partial x \partial y}} + P\cancel{\frac{\partial^2 V}{\partial x \partial y}} + \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \quad -(7)$$

Substracting (6) & (7) We get;

$$\boxed{\left(\frac{\partial S}{\partial x}\right)_y \cdot \left(\frac{\partial T}{\partial y}\right)_x - \left(\frac{\partial S}{\partial y}\right)_x \cdot \left(\frac{\partial T}{\partial x}\right)_y = \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x} \quad -(7)$$

(1) Let $x = T$, $y = V$

$\therefore \frac{\partial T}{\partial x} = 1, \frac{\partial V}{\partial y} = 1$ and $\frac{\partial T}{\partial y} = 0$ & $\frac{\partial V}{\partial x} = 0$

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

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

(2) Let $x = T$, $y = P$

$\therefore \frac{\partial T}{\partial x} = 1, \frac{\partial P}{\partial y} = 1$ & $\frac{\partial T}{\partial y} = 0, \frac{\partial P}{\partial x} = 0$

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

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

(3) Let $x = S$, $y = V$

$\therefore \frac{\partial S}{\partial x} = 1, \frac{\partial V}{\partial y} = 1$ & $\frac{\partial S}{\partial y} = 0, \left(\frac{\partial V}{\partial x}\right) = 0$

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

(4) Let $x = S$, $y = P$.

$\therefore \frac{\partial S}{\partial x} = 1, \frac{\partial P}{\partial y} = 1$ and $\frac{\partial P}{\partial x} = 0, \frac{\partial S}{\partial y} = 0$

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

Application of Max Well's thermodynamic relation.

(1) classius clapeyron's equ^n.

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

1st max well's equ^n ⟹

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

$$\left(\frac{dQ}{T\,dV}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\text{or, } \left(\frac{\partial Q}{dV}\right)_T = T\cdot\left(\frac{\partial P}{\partial T}\right)_V$$

Now, $\frac{dQ}{dV}$ represent the Latent heat per unit volume.

If L = Latent heat per unit mass

and $\partial V = V_2 - V_1$ then:

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

$$\text{or, } \boxed{\frac{\partial P}{\partial T} = \frac{L}{T(V_2-V_1)}}$$

(2) Prove that; $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\cdot\left(\frac{\partial V}{\partial T}\right)_P$

Ans:- $C_P - C_V = \left(\frac{T\,dS}{\partial T}\right)_P - \left(\frac{T\,\partial S}{\partial T}\right)_V$ ——— (A)

Let $S = f(T, V)$

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

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

$$\Rightarrow \left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T\cdot\left(\frac{\partial V}{\partial T}\right)_P \text{ ——— (B)}$$

using (B) in (A)

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

(4)

(3) Prove that $\underline{C_p - C_v = R}$.
for perfect gas.

$$PV = RT$$

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

$$\therefore \underline{C_p - C_v} = T \cdot \left(\frac{\partial P}{\partial T}\right)_P \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

$$= T \cdot R/V \cdot R/P = \frac{TR^2}{P.V}$$

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

(4) Prove that $\underline{C_p - C_v} = TE\alpha^2 V$.

$$\because \underline{C_p - C_v} = T \cdot \left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial T}\right)_P$$

Let $P = f(T \,\&\, V)$.

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

<u>At constant Press, $dP = 0$</u>

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

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

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

$$= -\frac{T}{\cancel{V}} \cdot \left(\frac{\partial P}{\partial V/V}\right)_T \cdot \left(\frac{\partial V/V}{\partial T}\right)^2 V^{\cancel{2}}$$

$$\Rightarrow \boxed{C_p - C_p = +TE \cdot \alpha^2 V}$$

(5) Prove that $E_S/E_T = \gamma$.

$\because E = -\frac{\partial P}{(\partial V/V)} = -V \cdot \left(\frac{dP}{\partial V}\right)$

$E = \frac{\text{Stress}}{\text{Strain}}$

$= \frac{P}{dV/V}$

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

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

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

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

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

Using thermodynamic relations

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

$$\frac{E_S}{E_T} = \frac{(\partial S/\partial T)_P}{(\partial S/\partial T)_V} = \frac{T(\partial S/\partial T)_P}{T(\partial S/\partial T)_V}$$

$$\frac{E_S}{E_T} = \frac{(\partial Q/\partial T)_P}{(\partial Q/\partial T)_V} = C_P/C_V$$

$\therefore \boxed{E_S/E_T = \gamma}$

6) Show that the ratio of adiabatic and ~~isothermal~~ isobaric coefficient of volume expansion is $\frac{1}{\gamma-1}$

The adiabatic and isobaric volume expansion are defined as:

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

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

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

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

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

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

$$\therefore \boxed{\frac{\alpha_S}{\alpha_P} = \frac{1}{\frac{C_P}{C_V} - 1} = \frac{1}{\gamma - 1}}$$

7) Prove that ratio of adiabatic and isochoric pressure coefficient of expansion is $\gamma/\gamma-1$

The adiabatic and isochoric pressure coefficient are defined as:

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

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

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

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

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

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

$$= \frac{C_P/C_V}{C_P/C_V - 1}$$

$$\therefore \boxed{\frac{B_S}{B_V} = \frac{\gamma}{\gamma - 1}}$$

(7) For Vander wall gas Prove that

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

The Vander Waal gas is given by

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

Differentiating ~~we get~~ at const volume.

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

Differentiating for constant Pressure.

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

$$\text{or, } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R/V-b.}{\frac{RT}{(V-b)^2} - \frac{2a}{V^3}}.$$

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

$$= T\cdot\frac{R}{(V-b)}\cdot\frac{R/V-b}{\frac{RT}{(V-b)^2} - 2a/V^3}$$

$$= \frac{R}{1 - \frac{2a}{V^3}\cdot(V-b)^2}$$

Neglecting b in compression to V We get

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