

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

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

$$\& dS = Tds \quad \text{--- (2)}$$

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

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

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

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

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

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

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

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

From equⁿ (3)

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

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 eqnⁿ 4 w.r to y and eqnⁿ 5 with respect to x. (2)

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

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

Subtracting (6) & (7) We get;

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Application of Maxwell's thermodynamic relation.

(1) classical clapeyron's eqn.

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

Let max well's eqn. =>

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

$$dQ = T ds$$

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

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

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

$$\text{Ans:- } C_p - C_v = \left(\frac{T ds}{\partial T}\right)_P - \left(\frac{T ds}{\partial T}\right)_V \quad \text{--- (A)}$$

Let $S = f(T, V)$

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

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

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

Using (B) in (A)

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

3) Prove that $C_p - C_v = R$.
for perfect gas.

$$PV = RT$$

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

$$\begin{aligned} \therefore C_p - C_v &= T \cdot \left(\frac{\partial P}{\partial T}\right)_P \cdot \left(\frac{\partial V}{\partial T}\right)_P \\ &= T \cdot R/V \cdot R/P = \frac{TR^2}{P \cdot V} \checkmark \end{aligned}$$

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

4) Prove that $C_p - C_v = T E \alpha^2 V$

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

Let $P = f(T, V)$

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

At constant Press, $dP = 0$

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

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

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

$$\Rightarrow \boxed{C_p - C_v = +T E \alpha^2 V \checkmark}$$

5) Prove that $E_s/E_T = \gamma$.

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

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

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

$$E = \frac{\text{Stress}}{\text{strain}} = \frac{P}{\Delta V/V}$$

$$\begin{aligned} \text{Now } \frac{E_s}{E_T} &= \frac{\left(\frac{\partial P}{\partial V}\right)_s}{\left(\frac{\partial P}{\partial V}\right)_T} \\ &= \frac{\left(\frac{\partial P}{\partial T}\right)_s \cdot \left(\frac{\partial T}{\partial V}\right)_s}{\left(\frac{\partial P}{\partial S}\right)_T \cdot \left(\frac{\partial S}{\partial V}\right)_T} \\ &= \frac{\left(\frac{\partial P}{\partial T}\right)_s \cdot \left(\frac{\partial T}{\partial V}\right)_s}{\left(\frac{\partial P}{\partial S}\right)_T \cdot \left(\frac{\partial S}{\partial V}\right)_T} \end{aligned}$$

Using thermodynamic relations

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

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

$$\frac{E_s}{E_T} = \frac{(\partial Q/\partial T)_P}{(\partial Q/\partial T)_V} = C_p/C_v$$

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

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

The adiabatic and isobaric volume expansion are defined as:

$$\alpha_s = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_s \quad \& \quad \alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p$$

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

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

$$= \frac{1}{\left(\frac{\partial p}{\partial s} \right)_V \cdot \left(\frac{\partial V}{\partial T} \right)_p} = \frac{1}{\left(\frac{\partial p}{\partial T} \right)_V \cdot \left(\frac{\partial T}{\partial s} \right)_V \cdot \left(\frac{\partial V}{\partial T} \right)_p}$$

$$= -T \left(\frac{\partial s}{\partial T} \right)_V / T \cdot \left(\frac{\partial p}{\partial T} \right)_V \cdot \left(\frac{\partial V}{\partial T} \right)_p$$

$$= \frac{\left(\partial s / \partial V \right)_V}{T \cdot \left(\frac{\partial p}{\partial T} \right)_V \cdot \left(\frac{\partial V}{\partial T} \right)_p} = \frac{c_v}{c_p - c_v}$$

$$\therefore \frac{\alpha_s}{\alpha_p} = \frac{1}{\frac{c_p}{c_v} - 1} = \frac{1}{\gamma - 1}$$

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:

$$\beta_s = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_s \quad \& \quad \beta_V = \frac{1}{p} \left(\frac{\partial p}{\partial T} \right)_V$$

$$\text{Now } \frac{\beta_s}{\beta_V} = \frac{\left(\partial p / \partial T \right)_s}{\left(\partial p / \partial T \right)_V}$$

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

$$= \frac{1}{\left(\frac{\partial V}{\partial s} \right)_p \cdot \left(\frac{\partial p}{\partial T} \right)_V}$$

$$= \frac{1}{\left(\frac{\partial V}{\partial T} \cdot \frac{\partial T}{\partial s} \right)_p \cdot \left(\frac{\partial p}{\partial T} \right)_V}$$

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

$$= \frac{C_p / C_v}{C_p / C_v - 1}$$

$$\therefore \frac{\frac{\partial s}{\partial V}}{\frac{\partial V}{\partial P}} = \frac{\gamma}{\gamma - 1}$$

⑦ For Vander wall gas Prove that
 $C_p - C_v = R \left(1 + \frac{2a}{VRT} \right)$
 The Vander wall gas is given by

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

Differentiating ~~the eq~~ at const volume.

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

Differentiating for constant pressure.

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

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

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

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

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

Neglecting b in comparison to V we get

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