Unit: 3

Maxwell's Thermodynamic Relations: Derivation of Maxwell's Relations. Application of Maxwell's relation to (1) Clausius Clapeyron equation, (2) Values of $C_p - C_v$. (3) TdS equations, (4) Joule-Kelvin coefficient for Ideal and Vander Waal gases, (5) change of temperature during Adiabatic process etc.

Phase Transition: First and second order phase transition with examples, Clausius Clapeyron Equation.

21/09/24.

Derivation of Maxwell's Thermodynamic relation:

From the first law of thermodynamic, we have –

$$dQ = dU + PdV$$

$$\Rightarrow dU = dQ - PdV$$

Again, from second law of thermodynamics, we have –

$$dQ = TdS$$

$$\therefore \; dU = TdS - PdV \quad \text{—} (1)$$

Let, U, S and V be the function of 2 independent variable x and y then –

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

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

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

Putting the value of dU, dS and dV in eqn (1), we get $\Rightarrow$

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

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

Equating the coefficient of dx and dy, we get ⇒

$$\left(\frac{\partial u}{\partial x}\right)_y = T\left(\frac{\partial s}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \quad \text{—(2)}$$

$$\left(\frac{\partial u}{\partial y}\right)_x = T\left(\frac{\partial s}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \quad \text{—(3)}$$

Differentiating eqⁿ (2) wrt 'y' and eqⁿ (3), wrt 'x', we get ⇒

$$\frac{\partial^2 u}{\partial y \partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial s}{\partial x}\right)_y + T\left(\frac{\partial^2 s}{\partial x \partial y}\right) - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\left(\frac{\partial^2 V}{\partial y \partial x}\right) \quad \text{—(4)}$$

$$\frac{\partial^2 u}{\partial x \partial y} = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial s}{\partial y}\right)_x + T\left(\frac{\partial^2 s}{\partial x \partial y}\right) - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\left(\frac{\partial^2 V}{\partial x \partial y}\right) \quad \text{—(5)}$$

Since du, ds and dV are perfect differentiates.

$$\therefore \quad \frac{\partial^2 u}{\partial y \partial x} = \frac{\partial^2 u}{\partial x \partial y} \; ; \; \frac{\partial^2 V}{\partial x \partial y} = \frac{\partial^2 V}{\partial y \partial x} \text{ and } \frac{\partial^2 s}{\partial x \partial y} = \frac{\partial^2 s}{\partial y \partial x}$$

So, from eqⁿ (4) and eqⁿ (5), we get ⇒

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

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

→

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x} \quad -(6)$$

This is the general eqn. for Maxwell's thermodynamic relation.

The different relation can be obtained by substituting the 4 variable S, P, T and V for x and y.

1. **First Relation:** putting $x = T$ and $y = V$

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

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

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

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

2. **Second Relation:** putting $x = T$ and $y = P$

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

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

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

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

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

✓3. **Third Relation:** Putting $x = S$; $y = V$

$$\frac{\partial S}{\partial x} = 1 \;;\; \frac{\partial S}{\partial y} = 0$$

$$\frac{\partial V}{\partial x} = 0 \;;\; \frac{\partial V}{\partial y} = 1$$

$$\text{Eq}^n(6) \Rightarrow \left(\frac{\partial T}{\partial V}\right)_S \cdot 1 - \left(\frac{\partial P}{\partial V}\right)_S \cdot 0 = \left(\frac{\partial T}{\partial S}\right)_V \cdot 0 - \left(\frac{\partial P}{\partial S}\right)_V \cdot 1$$

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

✓4. **Fourth Relation:** putting $x = S$; $y = P$

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

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

$$\text{Eq}^n(6) \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial S}{\partial S}\right)_P - \left(\frac{\partial P}{\partial P}\right)_S \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial S}{\partial P}\right)_S - \left(\frac{\partial P}{\partial S}\right)_P \left(\frac{\partial V}{\partial P}\right)_S$$

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

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

Application of Maxwell's Thermodynamic Relation:

✓1. Prove that $\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha$ where the symbols have their usual meaning.

↳ From, Maxwell's relation, we have—

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

→

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

Multiplying both sides by T, we get ⇒

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

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

$$\Rightarrow \boxed{\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P} \text{ --- (1) ; } [Q = TS$$

Now, from the definition of coefficient of volume, we have -

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

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

$$\therefore \text{Eq}^n (1) \Rightarrow \boxed{\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha}.$$

2. Show that - $C_P - C_V = TE\alpha^2 V$; where E is the bulk modulus of elasticity and α is the co-efficient of vol.^{m} expansion.

↳ From the definition of specific heat ~~and~~ at constant P and V, we have -

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

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

since, dS is a perfect diff. wrt T and V, we can write ⇒

→

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

Differentiating wrt 'T' ~~and~~ at constant 'P', we get-

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

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

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

$$\Rightarrow C_P - C_V = T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad \text{—(1)}$$

Again, P is a function of 'V' and 'T' also dP is a perfect differentiation.

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

If the process is isobaric then $dP = 0$

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

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

Also, from Maxwell's relation we have-

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{—(3)}$$

using eqⁿ(2) and eqⁿ(3) in eqⁿ(1); we get ⇒

$$C_P - C_V = T\left\{\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P\right\} \quad \left[\text{using eq}^n (3)\right.$$

$$\Rightarrow C_P - C_V = T\left\{-\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial V}{\partial T}\right)_P\right\} \quad \left[\text{using eq}^n (2)\right.$$

$$\Rightarrow C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 \quad \text{—(4)}$$

from the definition of Bulk modulus -

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

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

$$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = \frac{-E}{V} \quad \text{—(5)}$$

Also from the definition of vol.m expansion, we have-

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

$$\Rightarrow \alpha V = \left(\frac{\partial V}{\partial T}\right)_P \quad \text{—(6)}$$

using eq^n (5) and eq^n (6) in eq^n (4), we get ⇒

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

$$\Rightarrow \boxed{C_p - C_v = TE\alpha^2 V}$$ (Hence proved)

3. Derivation of Claussius Clayperon eq^n:

From Maxwell's Thermodynamic relation we have-

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

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

$$\Rightarrow \left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \quad \text{—(1)} \qquad [\partial Q = T\partial S$$

Here $\left(\frac{\partial Q}{\partial V}\right)_T$ represent the quantity of heat absorb or liberated per unit vol.m at constant temperature. So this quantity of heat absorb or liberated at constant temperature must be the latent heat and change is vol.m must be due to change in heat.

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If we consider unit mass of a substance and L be the latent heat when the substance change in V in V_1 and V_2 at constant T, then -

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

So, Eqⁿ (1) becomes ⇒

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

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

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

Which is Clausious - Clayperon equation.

4. Three Tds equation:

Depending on the choice of indipendent variable there are three Tds equation:

(a) **First Tds equation:** In this case we take T and V as independent variable of entropy s.

$$s = s(T, V)$$

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

$$\Rightarrow Tds = T\left(\frac{\partial s}{\partial T}\right)_V dT + T\left(\frac{\partial s}{\partial V}\right)_T dV$$

$$\Rightarrow Tds = \left(\frac{\partial Q}{\partial T}\right)_V dT + T\left(\frac{\partial s}{\partial V}\right)_T dV$$

$$\Rightarrow Tds = C_V dT + T\left(\frac{\partial s}{\partial V}\right)_T dV$$

using maxwell's relation, we have —

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

$$\therefore \boxed{TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV} \quad \text{---(1)}$$

(b) <u>Second TdS equation</u>: In this case we take T and P as independent variable of entropy S.

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

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

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

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

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

Now from Maxwell relation –

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

$$\therefore \boxed{TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP} \quad \text{---(2)}$$

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

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

$\therefore$ Eq^n (2) becomes $\Rightarrow$

$$\boxed{TdS = C_P dT - T\alpha V dP} \quad \text{---(3)}$$

(c) <u>Third TdS equation</u>: In this case P and V is independent variable of entropy S.

$$\therefore S = S(P, V)$$

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

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

$\rightarrow$

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

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

$$\Rightarrow \boxed{Tds = C_V \left(\frac{\partial T}{\partial P}\right)_V dP + C_P \left(\frac{\partial T}{\partial V}\right)_P dV} \quad \text{—(4)}$$

⇒ **Importance:** (To find the entropy of a substance from the directly measurable quantities).

✓5. **Change of temperature during adiabatic process:**

From Maxwell's thermodynamic relation, we have—

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

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_s = -T\left(\frac{\partial P}{\partial Q}\right)_V \quad ; \quad [\partial Q = T\partial s$$

Since increasing amount of heat at constant volᵐ always results in increase pressure $\left(\frac{\partial P}{\partial Q}\right)_V$ is positive hence the form $\left(\frac{\partial T}{\partial V}\right)_s$ should be negative i.e the temperature should decrease with increasing volume under condition of constant entropy or adiabatic process. So an adiabatic expansion must result in a fall of temperature.

Again from Maxwell's thermodynamic relation, we have—

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial s}\right)_P$$

$$\Rightarrow \left(\frac{\partial T}{\partial P}\right)_s = T\left(\frac{\partial V}{\partial Q}\right)_P$$

Since an increase in quantity of heat at constant P always results in increase in volume. So the —

→

term $\left(\frac{\partial V}{\partial Q}\right)_P$ is positive and $\left(\frac{\partial T}{\partial P}\right)_S$ must be positive. i.e temperature must increase with in increase in p under condition of constant entropy or adiabatic process. So as adiabatic compression always results an increase in temperature.

16. **Joule-Thomson expansion:** When a gas at constant high pressure is forced Porus plug to region of constant low pressure, the temperature of the escaping gas changes, this is called Joule-Thomson expansion.

During Joule-Thomson expansion enthalpy 'H' of the gas remains constant.

$$H = U + PV = \text{constant}$$

$$\therefore\ dH = dU + PdV + VdP = 0$$

But, $$dQ = dU + Pd\cancel{d}V$$

$$\therefore\ dQ + VdP = 0$$

$$\Rightarrow TdS + VdP = 0 \quad \text{——(1)}$$

[using 1st and 2nd law]

If we make entropy 's' as function of two independent variable T and P then the change in entropy can be expressed as –

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

$$\Rightarrow Tds = T\left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial P}\right)_T dP$$

$\therefore$ Eq^n (1) becomes $\Rightarrow$

$$T\left(\frac{\partial s}{\partial T}\right)_P dT + T\left(\frac{\partial s}{\partial P}\right)_T dP + Vdp = 0 \quad \text{——(2)}$$

Now, $T\left(\frac{\partial s}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P$; the specific heat at constant pressure.

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Also from Maxwell's relation.

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

$\therefore$ Eq^n (2) becomes $\Rightarrow$

$$C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP + V dp = 0$$

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

Joule-Thomson coefficient is given by-

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left\{T\left(\frac{\partial V}{\partial T}\right)_P - V\right\} \quad \text{---(3)}$$

This expression gives the change in temperature of a gas due to Joule-Thomson effect.

For a perfect gas the eq^n of state is $PV = RT$

Differentiating wrt 'T' keeping 'P' as constant we get $\Rightarrow$

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

$$\therefore T\left(\frac{\partial V}{\partial T}\right)_P = \frac{RT}{P} = \frac{PV}{P} = V$$

$\therefore$ from eq^n (3), we get $\Rightarrow$

$$\boxed{\mu = 0}$$

So Joule-Thomson coefficient for a perfect gas is zero.

For a real gas the eq^n of state is –

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

Differentiating wrt 'T' taking 'P' constant, we get $\Rightarrow$

$\rightarrow$

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

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

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

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

$\because$ $V >> b$ so we can neglect b and can write V^2 in place of $(V-b)^2$.

$$\therefore \left(\frac{\partial V}{\partial T}\right)_p = \frac{R(V-b)}{RT - \frac{2a}{V}}$$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_p = \frac{V-b}{T - \frac{2a}{VR}}$$

$$\therefore T\left(\frac{\partial V}{\partial T}\right)_p = \frac{T(V-b)}{T - \frac{2a}{VR}} = \frac{V-b}{1-\frac{2a}{RTV}}$$

$$\Rightarrow T\left(\frac{\partial V}{\partial T}\right)_p = (V-b)\left(1-\frac{2a}{RTV}\right)^{-1}$$

$$\Rightarrow T\left(\frac{\partial V}{\partial T}\right)_p \doteq (V-b)\left(1+\frac{2a}{RTV}\right)$$

Expanding binomially and neglecting higher order

$$\Rightarrow T\left(\frac{\partial V}{\partial T}\right)_p = V-b+\frac{2a}{RT} - \frac{2ab}{RTV}$$

$$\Rightarrow T\left(\frac{\partial V}{\partial T}\right)_p = V-b+\frac{2a}{RT} \quad ;$$

$\frac{2ab}{RTV}$ can be neglected since a and b very small

$$\Rightarrow T\left(\frac{\partial V}{\partial T}\right)_P - V = \frac{2a}{RT} - b$$

Substituting the value in eq^n (3), we get $\Rightarrow$

$$\boxed{\mu = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)}$$

This is the expression for Joule - Thomson co-efficient for real gas.

On this expression it is clear that if $\frac{2a}{RT} > b$ i.e, $T < \frac{2a}{Rb}$ then $\mu = \left(\frac{\partial T}{\partial P}\right)_H$ is positive. Since ∂P is negative quantity so ∂T also should be negative hence the gas should be cool passing through the Porous plug.

Again, $\frac{2a}{RT} < b$ and $T > \frac{2a}{Rb}$ then μ is negative so ∂T will be positive because ∂P is always negative thus the gas will be heated up on passing through Porous plug.

Now, if $\frac{2a}{RT} = b$ i.e $T = \frac{2a}{bR}$ then $\mu = 0$ i.e the gass passing through the Porous plug will show no change in temperature.

The temperature at which Joule-Thomson coefficients changes in sign is known as temperature of inversion which is denoted by $\boxed{T_i = \frac{2a}{Rb}}$.

Q. Show that for a homogeneous fluid $C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$ and hence prove that-

(i) For a perfect gas- $C_p - C_v = R$

(ii) For a Vander Waal's gas- $C_p - C_v = R\left(1 + \frac{2a}{RTV}\right)$.

↳ The specific heat at constant P and constant V are given by-

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \longrightarrow (1) \quad \left[\because \partial Q = T\partial S\right]$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \longrightarrow (2)$$

If entropy has the function of 'T' and 'V' then-

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

Differentiating the above eq^n at constant 'P' and multiply it with 'T', we get ⇒

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

$$\Rightarrow C_p = C_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \longrightarrow (3) \quad \left\{\text{using eq}^n (1) \text{ and eq}^n (2)\right\}$$

using Maxwell's relation, we have-

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

So, eq^n (3) becomes ⇒

$$C_p - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \longrightarrow (4)$$

(i) For a perfect gas $PV = RT$,

→

Differentiating 'P' wrt 'T' at constant 'V', we get ⇒

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

Again differentiating 'V' wrt 'T' at constant P ⇒

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

Substituting the values in eq^n (4), we get ⇒

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

$$\Rightarrow C_p - C_v = \frac{R(RT)}{PV}$$

$$\Rightarrow \boxed{C_p - C_v = R} \quad [\because RT = PV$$

(ii) For Vanderwaal's gas, we have–

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

Differentiating wrt 'T' at constant 'V', we get ⇒

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

Again, differentiating wrt 'T' at constant 'P', we get ⇒

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

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

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

substituting the values of $\left(\frac{\partial P}{\partial T}\right)_V$ and $\left(\frac{\partial V}{\partial T}\right)_P$ in eqn. (4), we get ⇒

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

$$\Rightarrow C_p - C_V = \frac{T\frac{R^2}{(V-b)^2}}{\frac{RT}{(V-b)^2} - \frac{2a}{V^3}}$$

Dividing numerator and denominator by $\frac{RT}{(V-b)^2}$

$$\Rightarrow C_p - C_V = \frac{R}{1 - \frac{2a(V-b)^2}{RTV^3}}$$

$$\Rightarrow C_p - C_V = \frac{R}{1 - \frac{2aV^2}{RTV^3}} \qquad [\because b << V$$

$$\Rightarrow C_p - C_V = \frac{R}{1 - \frac{2a}{RTV}}$$

$$\Rightarrow C_p - C_V = R\left(1 - \frac{2a}{RTV}\right)^{-1}$$

$$\Rightarrow \boxed{C_p - C_V = R\left(1 + \frac{2a}{RTV}\right)}$$

Expanding binomially and neglecting higher order.

✓**Phase:** A phase is defined as the system which is homogeneous having defined boundaries.

A substance usually state either in solid liquid or in gaseous state, each of these state are called phase.

✓**Phase Transition:** The process in which the thermodynamic system changes from one state to another with different physical properties is called phase transition.

✓**First order transition:** The phase transition in which temperature and pressure remains constant while the entropy and vol^n changes and also the first order derivatives of Gibb's function changes discontinuously is known as first order transition.

Example: Melting, vapourization, sublimation.

✓**Clausius Clapeyron equation of first order transition:**

Let us consider 1 mole of a substance undergoes a change from phase i to phase f.

Now, from 1st Tds equation, we have =>

$$T\,ds = C_p\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \quad —(1)$$

Assuming that various P and T at which phase transition occurs obeys a relation where P is function of T only (independent of V).

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

Again for first order transition –

$dT = 0$ and $C_p = \infty$ (undefined), So, eq^n (1) becomes ⇒

$$T(S_f - S_i) = T\frac{dP}{dT}(V_f - V_i)$$

and the left hand side of the equation is the latent heat per mole which is represented by-

$$L = T\frac{dP}{dT}(V_f - V_i)$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{L}{T(V_f - V_i)}}$$

which is Clausius Clapeyron's equation.

✓Second Order phase transition:

The transition in which there is no change of entropy and volume but it's discontinuouty appear in specific heat and constant P and isobaric vol^m expansion. i.e, the first order derivative of Gibb's function are continuous but second order derivative shows discontinuous state is known as 2nd order phase transition.

eg: The transition of normal He (He I) to superfluid (He II).

✓Ehrenfest Equation of 2nd order phase transition:

In a second order phase transition the vol^m and entropy remains constant. The constancy of entropy is represented by - $S_1 = S_2$ —(1). ; at temp. T and pressure P

where the two phases are represented by 1 and 2

as the temperature is raised infinitesimally from T to (T+dT) and pressure from P to (P+dP)

then - $S_1 + dS_1 = S_2 + dS_2$ —(2)

So, from eqⁿ(1) and eqⁿ(2); we get ⟹

$$dS_1 = dS_2 \quad \text{—(3)}$$

Now, expressing entropy as a function of T and P, we get ⟹

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

$$\Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_P dT - \left(\frac{\partial V}{\partial T}\right)_P dP \quad \left\{\text{using Maxwell's relation}\right\}$$

$$\Rightarrow dS = \frac{C_P}{T} dT - V\alpha\, dP \quad \text{—(4)} \; ; \left[\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right]$$

Where, $C_P = T\left(\frac{\partial S}{\partial T}\right)_P$ is the specific heat at constant pressure is the isobaric volᵐ expansion.

Since volᵐ 'V' is the same for both the phases.

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

$$\text{and } \; dS_2 = \left(\frac{C_{P_2}}{T}\right) dT - V\alpha_2 dP$$

using eqⁿ(3), we can write ⟹

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

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

$$\Rightarrow \boxed{\left(\frac{dP}{dT}\right)_S = \frac{C_{P_1} - C_{P_2}}{(\alpha_1 - \alpha_2) TV}} \quad \text{—(5)}$$

Again starting from the combination of volᵐ i.e $V_1 = V_2$, we get for infinitisimaly small -

$$dV_1 = dV_2 \quad \text{—(6)}$$

Now expressing V as a function of T and P we get ⇒

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

$$\Rightarrow dV = \alpha V dT - V K_T \, dP \quad \text{——} (7)$$

Here, $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ is the bulk modulus of elasticity at constant temperature using (6) and (7) we can write ⇒

$$\alpha_1 V dT - V K_{T_1} dP = \alpha_2 V dT - V K_{T_2} dP$$

$$\Rightarrow (\alpha_1 - \alpha_2) V dT = V(K_{T_1} - K_{T_2}) \, dP$$

$$\Rightarrow \boxed{\left(\frac{dP}{dT}\right)_V = \frac{\alpha_1 - \alpha_2}{K_{T_1} - K_{T_2}}} \quad \text{——} (8)$$

Eqⁿ (5) and (8) are known as Ehrenfest's eqⁿ of 2nd order transition.

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