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Topic:

Maxwell's relations and Applications

2nd Law of Thermodynamics

Frequently Asked Numerical:

Solved Problems and Problems in exercise of Heat & Thermodynamics, Author A. B. Gupta, H.P Roy, and Published by: Books & Allied Pvt. Ltd. (2018).

References:

i. *Heat & Thermodynamics, Author A. B. Gupta, H.P Roy, Published by: Books & Allied Pvt. Ltd. (2018)*
ii. *Theory & Experiment on Thermal Physics, Author-P. K. Chakraborty, Published by: Central*

This study material is only class-note. This class-note is prepared by following the reference books. Students should read the reference books for better knowledge.

Link to Audio visual Lectures (e-Lectures) given by Distinguish Professors of Foreign Universities:

i. https://www.youtube.com/watch?time_continue=2&v=i-bo0DoWgqA&feature=emb_title
ii. https://www.youtube.com/watch?v=RXo9SShMHvE
iii. https://www.youtube.com/watch?v=aDXBo0FtALA&list=PLwdnzlV3ogoVnCnIfjDHng_8biZSUEYtK

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Thermodynamic Relation

The relation among pressure (P), volume (V), temperature (T) & entropy (S) of a thermodynamic system, from the two laws of thermodynamics known as thermodynamic relation. Scientist Maxwell first derived the thermodynamic laws. Therefore the laws known as Maxwell's thermodynamic relation.

Ground → Relation 1 | Floor → Relation 2 | Upper → Relation 3 | Home → Relation 4

1st Relation

$$G = H - TS$$

$$\Rightarrow G = U + PV - TS$$

$$\Rightarrow dG = du + pdV + Vdp - Tds - SdT$$

$$\Rightarrow dG = Tds + Vdp - Tds - SdT$$

$$\Rightarrow dG = Vdp - SdT$$

Since dG is a perfect differential

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

$dz = Mdx + Ndy$
dz is a perfect differential
$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial M}{\partial y}\right)_x$

2nd Relation

$$F = U - TS$$

$$\Rightarrow df = du - Tds - SdT$$

$$= du - du - pdV - SdT$$

$$= -pdV - SdT$$

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Since df is a perfect differential

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

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

3rd Relation

$$dQ = du + pdv$$

$$TdS = du + pdv$$

$$du = TdS - pdv$$

Since du is a perfect differential

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

4th Relation

$$H = U + pV$$

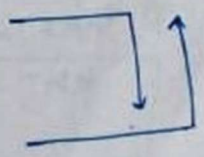
$$\Rightarrow dH = du + pdv + Vdp$$

$$\Rightarrow dH = TdS + Vdp$$

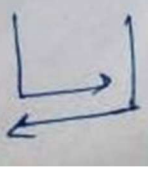
Since dH is a perfect differential

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

Method:-

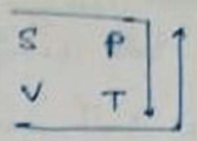


up-down arrow = -Ve



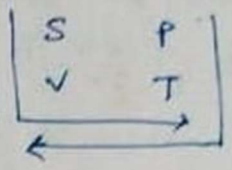
parallel arrow = +Ve

1st Relation



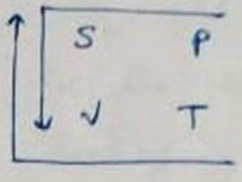
$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

2nd Relation



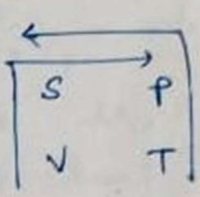
$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

3rd Relation



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

4th Relation



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

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

Soln We have from 1st Relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

multiplying both sides by T

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

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

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

Putting the value of $\left(\frac{\partial V}{\partial T}\right)_P$ in eqn. (1) we get.

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

Interpretation of 1st relation:

(a) We have found that $\left(\frac{\partial Q}{\partial P}\right)_T = -TV\alpha$

The substances that expands on heating the (α) is +ve for this case

We have, $\left(\frac{\partial Q}{\partial P}\right)_T = -ve$

Therefore, if $dP = +ve$ & $dQ = -ve$

It states that heat generates on compression.

(b) α is -ve for the substances which contracts on heating

$\therefore \left(\frac{\partial Q}{\partial P}\right)_T = +ve$

If $dP = +ve$ $dQ = +ve$

It states that heat absorbance or cooling is produced due to compression.

Clausius - Clapeyron equation:-

From Maxwell's 2nd Relation we have,

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

multiplying both side by T we get,

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

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

$\left(\frac{\partial Q}{\partial V}\right)_T$ = Quantity of heat absorbed per unit increase in volume at constant temperature.

The quantity of absorbed heat at constant temperature per unit mass is the Latent heat.

Here, $\partial Q = L$ (Latent heat)

and $\partial V = V_2 - V_1$

V_1 = initial volume of unit mass of substance

V_2 = final volume of unit mass of substance

$$\therefore \frac{\partial P}{\partial T} = \frac{L}{T(V_2 - V_1)}$$

$$\left(\frac{\partial P}{\partial T}\right)_{sat} = \frac{L}{T(V_2 - V_1)}$$ → Clausius Clayperon Equation.

Interpretation;

(i) $V_2 - V_1 = -ve$ for the substance which contracts in melting.

$$\therefore \left(\frac{\partial P}{\partial T}\right) = -ve$$

When $(\partial P) = +ve$ $\partial T = -ve$

It states that increase in pressure decreases the melting point.

(ii) $V_2 - V_1 = +ve$ for the substances which expands in melting

$$\therefore \left(\frac{\partial P}{\partial T}\right) = +ve$$

when, $\partial P = +ve$; $\partial T = +ve$

It states that increases the pressure increases the melting point.

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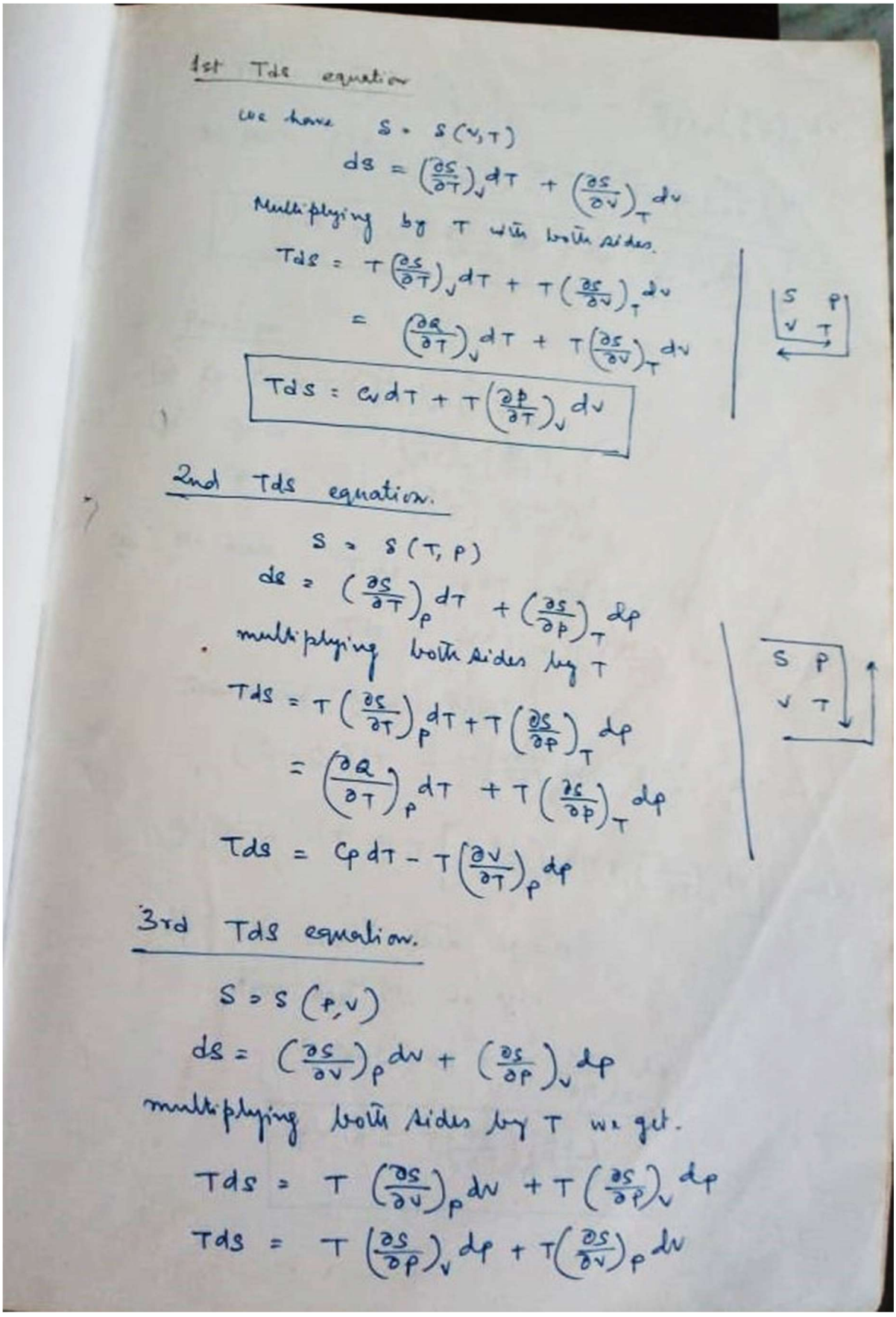

1st Tds equation

We have $S = S(V,T)$

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

Multiplying by T with both sides.

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

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

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

S P
V T

2nd Tds equation.

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

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

multiplying both sides by T

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

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

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

S P
V T

3rd Tds equation.

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

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

multiplying both sides by T we get.

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

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

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$\Rightarrow Tds = T\left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial T}{\partial p}\right)_v dp + T\left(\frac{\partial s}{\partial T}\right)_p \left(\frac{\partial T}{\partial v}\right)_p dv$

$\Rightarrow Tds = \left(\frac{\partial q}{\partial T}\right)_v \left(\frac{\partial T}{\partial p}\right)_v dp + \left(\frac{\partial q}{\partial T}\right)_p \left(\frac{\partial T}{\partial v}\right)_p dv$

$\therefore \boxed{Tds = C_v \left(\frac{\partial T}{\partial p}\right)_v dp + C_p \left(\frac{\partial T}{\partial v}\right)_p dv}$

Relations

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

(b) $C_p - C_v = -T\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v^2$

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

(a) We have.

$Tds = C_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp \quad \text{—(i)}$

$Tds = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dv \quad \text{—(ii)}$

Subtracting from (i) & (ii)

$(C_p - C_v)dT - T\left(\frac{\partial v}{\partial T}\right)_p dp - T\left(\frac{\partial p}{\partial T}\right)_v dv = 0$

$\Rightarrow (C_p - C_v)dT = T\left[\left(\frac{\partial v}{\partial T}\right)_p dp + \left(\frac{\partial p}{\partial T}\right)_v dv\right] \quad \text{—(3)}$

If p is const^{n}, then $dp = 0$

from eq^{n} (3) we get

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

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

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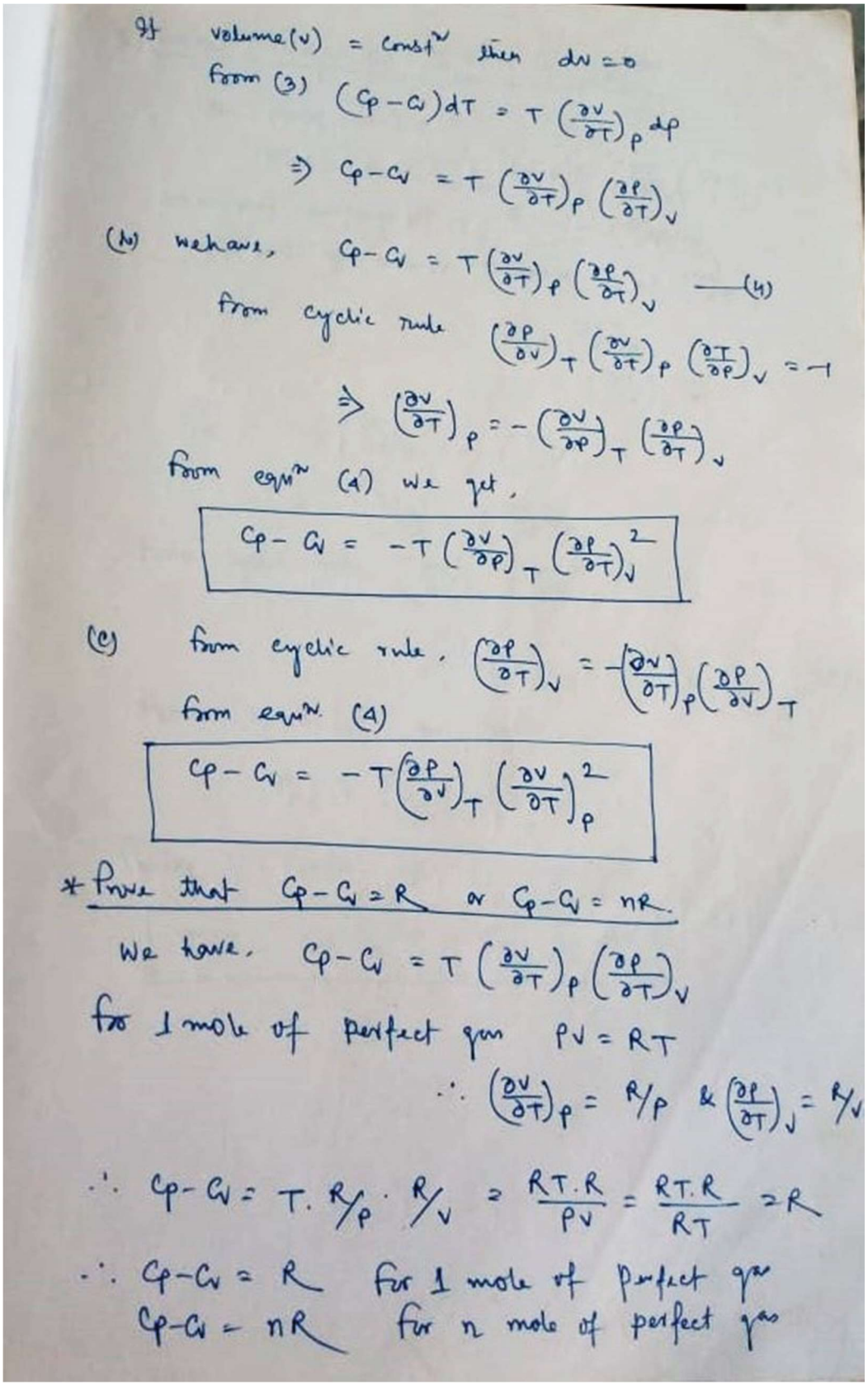

If volume(v) = const^{n} then $dv = 0$

from (3) $(C_p - C_v)dT = T\left(\frac{\partial v}{\partial T}\right)_p dp$

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

(b) we have, $C_p - C_v = T\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_v$ ——(4)

from cyclic rule $\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v = -1$

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

from eqn^{n} (4) we get,

$$\boxed{C_p - C_v = -T\left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_v^2}$$

(c) from cyclic rule, $\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial p}{\partial v}\right)_T$

from eqn^{n} (4)

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

* Prove that $C_p - C_v = R$ or $C_p - C_v = nR$.

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

for 1 mole of perfect gas $pv = RT$

$\therefore \left(\frac{\partial v}{\partial T}\right)_p = R/p$ & $\left(\frac{\partial p}{\partial T}\right)_v = R/v$

$\therefore C_p - C_v = T \cdot R/p \cdot R/v = \frac{RT \cdot R}{pv} = \frac{RT \cdot R}{RT} = R$

$\therefore C_p - C_v = R$ for 1 mole of perfect gas

$C_p - C_v = nR$ for n mole of perfect gas