Date:

FIRST TdS EQUATION:

(1)

Consider entropy of a system is a function of temp T and volume V

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

differentiating

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

multiplying both sides by T

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

The second law of thermodynamics is

$$dQ = TdS$$

at constant volume we can write as

$$T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{dQ}{dT}\right)_V = C_V \quad \text{—} (2)$$

putting value from (2) in (1)

$$TdS = C_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \quad \text{—} (3)$$

Now applying ~~function~~ condition of exact differentials to eq

$$dF = -SdT - PdV$$

to get maxwell ~~equation~~ relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{—} (4)$$

Important: putting value from eq (4) in (3)

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Q, V, T, P

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$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \quad \text{--- (5)}$$

Eq is called first TdS equation

--- other form

Using mathematical theorem

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

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

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

$$= K\beta$$

$$= \frac{\beta}{k} \qquad \because K = \frac{1}{k}$$

$$k = \frac{1}{K} = -\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

using this value in eq (5), then first TdS eq becomes

$$TdS = C_V dT + \frac{\beta}{k} \cdot T dV$$

2nd TdS equation:

Consider entropy of a system is a function of temperature T & pressure P

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

differentiating

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

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xing by both sides T

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \quad \text{—} ①$$

by 2nd law of thermodynamic

$$dQ = TdS$$

at constant pressure, we can write

$$T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_P \quad \text{—} ②$$

putting value from eq ② in ①

$$TdS = C_P \, dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \quad \text{—} ③$$

now applying condition of Gibbs

$$dG = -SdT + VdP$$ to get maxwell relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{—} ④$$

putting value from ④ in ③ we have

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

This is called 2nd TdS equation

3rd TdS equation:

Consider entropy of a system is a function of pressure P & volume V

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

differentiating

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

multiply by T

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV \quad \text{—(1)}$$

by 2nd law of thermodynamics

$$dQ = TdS$$

at constant

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

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

by mathematical theorem

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

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

Putting eq (2) in (1)

$$TdS = -C_v \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P dP + C_P V \left(\frac{\partial T}{\partial V}\right)_P \frac{1}{V} dV$$

$$= C_v \left[-\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T V \left(\frac{\partial T}{\partial V}\right)_P dP + \frac{C_P}{V\beta} dV \right]$$

$$= \frac{C_v k}{\beta} dP + \frac{C_P}{V\beta} dV$$

where $\beta =$

$k =$

This is 3rd TdS equation

3 Helmholtz free energy F is defined as $F = U - TS$ — (1)
where U is internal energy, T is absolute temp & S is entropy.

The internal energy U might be thought of as the energy required to create a system in the absence of changes in temperature or volume. But if the system is created in an environment of temp T then some of energy can be obtained by spontaneous heat transfer from the environment to system.

The amount of this spontaneous energy transfer is TS, where S is the final entropy of system

for an infinitesimal reversible process diff eq (1)

$$dF = dU - TdS - SdT$$

as $dQ = dU + PdV$

$$\Rightarrow dU = dQ - PdV$$

putting value of dU in above eq

$$dF = dQ - PdV - TdS - SdT$$

as $dQ = TdS$

so

$$dF = \cancel{TdS} - PdV - \cancel{TdS} - SdT$$

$$dF = -PdV - SdT$$

Important: for reversible isothermal process

T = constant so $dT = 0$