Qu. Discuss TdS Equation

Ans. The relations between the thermodynamic properties of a system are traced to the combined form of the first and second laws. The actual derivation may be done in a variety of ways. The simplest and most methodical procedure is to make the TdS equations and the energy equations the starting point. The three Tds equations are obtained by expressing the specific entropy as a function of the pairs of variables, (T, V), (T, P) and (P,V) .

(i) **Taking entropy S as a function of volume V and temperature T i.e. , S= f(V,T)**

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

The 1st term of the right side of this equation is expressed in terms of C_V, the specific heat at constant volume i.e. the volume becomes constant, hence change in volume dV = 0, now

$$T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{T\partial S}{\partial T}\right)_V = \left(\frac{\partial Q_{rev}}{\partial T}\right)_V = C_V \qquad (2)$$

Eq. (1) reduces to

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

According to Maxwell's relation

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

Hence, Eq. (3) reduces to

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad (4)$$

This is known as 1st TdS equation.

(ii) Taking entropy S as a function of Pressure P and Temperature T. i.e. S= f(P,T)

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \qquad (5)$$

The 1st term of the right side of this equation is expressed in terms of C_P, the specific heat at constant pressure i.e. the volume becomes constant, hence change in pressure dP = 0, Now

$$T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{T\partial S}{\partial T}\right)_P = \left(\frac{\partial Q_{rev}}{\partial T}\right)_P = C_P \qquad (6)$$

The Eq. (5) reduces to

$$TdS = C_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \qquad (7)$$

According to Maxwell's thermodynamic relation

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

Hence Eq. (7) reduces to

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \qquad (8)$$

This is 2nd TdS equation.

(iii) Taking entropy S as a function of Pressure P and volume V. i.e

S= f(P,V)

$$TdS = T\left(\frac{\partial S}{\partial P}\right)_V dP + T\left(\frac{\partial S}{\partial V}\right)_P dV \qquad (9)$$

Now,

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

$$= \frac{C_V}{T}\left(\frac{\partial T}{\delta P}\right)_V$$

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

$$= \frac{C_P}{T}\left(\frac{\partial T}{\delta V}\right)_P$$

Putting these value in Eq. (4), Eq.(8) and Eq. (10), we get

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

$$\mathrm{TdS} = \mathrm{C_V}\left(\frac{\partial T}{\delta P}\right)_{\mathrm{V}} \mathrm{dP} + \mathrm{C_P}\left(\frac{\partial T}{\delta V}\right)_{\mathrm{P}} \mathrm{dV} \qquad (10)$$

This is 3rd TdS equation.

These three TdS equations also expressed in terms of isobaric coefficient of volume expansion

$$\beta_{\mathrm{P}} = \frac{1}{\mathrm{V}}\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{P}} \qquad (11)$$

And in terms of isothermal compressibility

$$\mathrm{K_T} = -\frac{1}{\mathrm{V}}\left(\frac{\partial \mathrm{V}}{\partial P}\right)_{\mathrm{T}} \qquad (12)$$

From Eq. (11) and Eq.(12), the ratio

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

The TdS equation may be written as

$$\mathrm{TdS} = \mathrm{C_V dT} + \mathrm{T}\left(\frac{\partial \mathrm{P}}{\partial \mathrm{T}}\right)_{\mathrm{V}} \mathrm{dV} = \mathrm{C_V}\ \mathrm{dT} + \frac{\mathrm{T}\beta_{\mathrm{P}}}{\mathrm{K_T}}\mathrm{dV} \qquad (13)$$

$$\mathrm{TdS} = \mathrm{C_P dT} - \mathrm{T}\left(\frac{\partial V}{\partial T}\right)\mathrm{dP} = \mathrm{C_P dT} - \mathrm{TV}\beta_P\ \mathrm{dP} \qquad (14)$$

$$\mathrm{TdS} = \mathrm{C_V}\left(\frac{\partial T}{\delta P}\right)_{\mathrm{V}} \mathrm{dP} + \mathrm{C_P}\left(\frac{\partial T}{\delta V}\right)_{\mathrm{P}} \mathrm{dV} = \mathrm{C_V}\frac{\mathrm{K_T}}{\beta_P}\mathrm{dP} + \frac{\mathrm{C_P}}{\beta_P V}\mathrm{dV} \qquad (15)$$

The energy Equations

The change in internal energy in an infinitesimal process is given by

$$\mathrm{dU} = \mathrm{TdS} - \mathrm{PdV}$$

Taking T and V as independent variable gives

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

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

Equating the coefficients of dV, we get

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P \tag{16}$$

From Maxwell's relations

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

In terms of isobaric coefficient of volume expansion β_P and isothermal compressibility K_T

$$\left(\frac{\partial U}{\partial V}\right)_T = T\frac{\beta_P}{K_T} - P \tag{17}$$

The Qu. (17) is called first energy equation. It is some times called the thermodynamic equation of state because the right side can be computed from the equation of the system from measured values of β_P, K_T and P.

The 2nd energy equation is obtained on taking T and P as independent variables. From 1st law of thermodynamics

dU = TdS - PdV .

Now,

$$\left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP - P\left(\frac{\partial V}{\partial T}\right)_P dT - P\left(\frac{\partial V}{\partial P}\right)_T dP \tag{18}$$

Or

$$\left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP = [T\left(\frac{\partial S}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P]dT + [T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T]dP \tag{19}$$

Equating the coefficients of dT and dP, we get

$$\left(\frac{\partial U}{\partial T}\right)_P = [T\left(\frac{\partial S}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P] \tag{20}$$

$$\left(\frac{\partial U}{\partial P}\right)_T = [T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T] \tag{21}$$

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