# THERMODYNAMIC RELATIONS :-

1. Exact Differentials.
2. Maxwell's Equations.
3. coefficient of Volume Expansion.
4. Isothermal compressibility.
5. Ratio of Co-Efficient of Volume Expansion ($\beta$) and isothermal compressibility ($K$).
6. Specific Heat Relations.
7. Ratio of Specific Heat Capacities.
8. Internal Energy Relations.
9. Entropy Relations (T ds Equations)
10. Enthalpy Relations.

## (2) Maxwell's Equations :-

The Maxwell's equations relate entropy to the three directly measurable properties $p, v$ and $T$ for pure simple compressible substances.

From first law of thermodynamics.

$$Q = W + \Delta U$$

$$Q = \Delta u + W.$$

$$T ds = du + p.dv. \qquad \left(\because ds = \frac{Q}{T} \text{ by second law of thermodynamics}\right)$$

$$du = T ds - p.dv. \quad \text{———} (1) \qquad (W = P dv \text{ by first law of thermodynamics})$$

We know that,

$$h = u + pv.$$

$$dh = du + d(pv).$$

$$dh = du + v.dp + p.dv. \text{———} (2) \qquad \because uv = uv' + vu'.$$

Substituting the value $du$ in equation (2).

$$dh = T.ds - \cancel{p dv} + v dp + \cancel{p dv}.$$

$$dh = T.ds + v.dp. \quad \text{———} (4).$$

By Helmotz's function :-

$$a = u - Ts.$$

$$da = du - d(Ts).$$

$\because uv = uv' + vu'$.

$d(uv) = u dv + v du$.

$$da = du - T.ds - s.dT. \quad \text{—— (4)}$$

Substituting the value of du in equation (4).

$$da = T.\cancel{ds} - P.dv - T.\cancel{ds} - s.dT.$$

$$da = -P dv - s.dT. \quad \text{—— (5)}$$

By Gibb's functions,

$$G = h - \cancel{d}Ts.$$

$$dg = dh - d(Ts).$$

$$dg = dh - Tds - s.dT. \quad \text{—— (6)}$$

Sustituting the value of dh in equation (6).

$$dg = T\cancel{ds} + v.dp - \cancel{T}ds - s.dT.$$

$\because dh = T.ds + V.dp$.

$$dg = v.dp - s.dT \quad \text{—— (7)}.$$

By inverse exact different we can write equation (7) as.

$$du = T.ds - P.dv.$$

$$\left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_V. \quad \text{—— (8)}$$

Similarly equation (3)

$$dh = T.ds + v.dP.$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial V}{\partial s}\right)_P. \quad \text{—— (9)}$$

Similarly, equation (5) can be written as,

$$da = -P dV - s.dT.$$

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial s}{\partial V}\right)_T \quad \text{—— (10)}.$$

Similarly equation (1) can be written as,

$$dg = v\,dp - s\,dT.$$

$$\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T \quad \text{———} (11).$$

These equation 8, 9, 10 and 11 are Maxwell's equation.

## (7) Ratio of Specific Heat Capacities :-

$$C_p = T\left(\frac{\partial s}{\partial T}\right)_p \quad \text{———} (1)$$

$$C_v = T\left(\frac{\partial s}{\partial T}\right)_v \quad \text{———} (2)$$

Dividing equation (1) by (2).

$$\gamma = \frac{C_p}{C_v} = \frac{T\left(\frac{\partial s}{\partial T}\right)_p}{T\left(\frac{\partial s}{\partial T}\right)_v} = \frac{\left(\frac{\partial s}{\partial T}\right)_p}{\left(\frac{\partial s}{\partial T}\right)_v}.$$

$$\boxed{\gamma = \left(\frac{\partial s}{\partial T}\right)_p \left(\frac{\partial T}{\partial s}\right)_v}$$

## (9) Tds Equations (Entropy Relations) :-

The entropy (s) of a pure substance can be expressed as a function of temperature (T) and pressure (P).

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

$$ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T \cdot dp$$

and,

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

$$\boxed{\left(\frac{\partial s}{\partial T}\right)_p = \frac{C_p}{T}}$$

From Maxwell equation (11) we know that,

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

substituting in equation (ds).

$$ds = \frac{C_p}{T}\,dT - \left(\frac{\partial v}{\partial T}\right)_p \cdot dp \quad \text{———} (1).$$

Multiplying by T on both side of the equation.

$$T.ds = \cancel{T}\frac{C_p}{\cancel{T}}dT - T.\left(\frac{\partial V}{\partial T}\right)_P.dp.$$

$$\boxed{T.ds = C_p.dT - T.\left(\frac{\partial V}{\partial T}\right)_P.dp} \quad \text{--- (2).}$$

This is known as the first form of entropy equation (or) the first T.ds equation.

By considering the entropy of a pure substance as a function of temperature and specific volume,

$$S = f(T, v)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_v dT + \left(\frac{\partial s}{\partial v}\right)_T.dv.$$

we know that,

$$C_v = T.\left(\frac{\partial s}{\partial T}\right)_v.$$

$$\boxed{\frac{C_v}{T} = \left(\frac{\partial s}{\partial T}\right)_v}$$

From Maxwell Equations (10), we know that,

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v.$$

Substituting in ds equation,

$$ds = \frac{C_v}{T}.dT + \left(\frac{\partial P}{\partial T}\right)_v.dv.$$

Multiplying by T, on both sides.

$$T.ds = \cancel{T}.\frac{C_v}{\cancel{T}}.dT + T\left(\frac{\partial P}{\partial T}\right)_v.dv.$$

$$\boxed{T.ds = C_v.dT + T\left(\frac{\partial P}{\partial T}\right)_v.dv} \quad \text{--- (3).}$$

This is known as the second form of entropy equation (or), the second T.ds equation.