

Thermodynamic Potentials  $\rightarrow$  The four functions  $U, H, F$  and  $G$  play a role analogous to that played by the potential energy for a mechanical system, they are called thermodynamic potentials which is min for stable state.

Maxwell Thermodynamic Relations : The changes in  $U, F, H, G$  during an infinitesimal change are given by

$$dU = Tds - PdV \quad \text{--- (31)}$$

$$dH = Tds + VdP \quad \text{--- (32)}$$

$$dF = -PdV - SdT \quad \text{--- (33)}$$

$$dG = VdP - SdT \quad \text{--- (34)}$$

Note that variables on right hand side of these equations are  $P, V, S$  and  $T$

1. Internal Energy or Intrinsic Energy  $\rightarrow$  Let  $dQ$  be the amount of heat energy absorbed by a system and  $dW = PdV$  be the amount of work done by system in going <sup>from</sup> initial state to final state, then change in internal energy of system is given by

$$dU = dQ - dW$$

But

$$dQ = Tds \text{ and } dW = PdV$$

$$dU = Tds - PdV \quad \text{--- (35)}$$

Diff. the internal energy (U) partially w.r.t. the variables V and S

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

Since dU is a perfect differential, so we can write

$$\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right) = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)$$

Using eqn. (1) we get

$$\left(\frac{\partial P}{\partial S}\right)_V = - \left(\frac{\partial T}{\partial V}\right)_S \text{ --- (37)}$$

This is first Maxwell's thermodynamical relation.

2. Helmholtz function (F) :-

Helmholtz function or Helmholtz free energy is defined as

$$F = U - TS \text{ --- (38)}$$

Diff. eqn. (38), we get

$$dF = dU - TdS - SdT$$

But

$$dU = TdS - PdV$$

$\therefore$

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

or

$$dF = -PdV - SdT \text{ --- (39)}$$

Diff. F partially w.r.t. the variables V and T, we get

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \text{ and } \left(\frac{\partial F}{\partial T}\right)_V = -S \text{ --- (40)}$$

Since dF is a perfect differential, so

$$\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right)$$

Using eqn. (40), we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \text{ --- (41)}$$

This is third Maxwell's thermodynamical relation

3. Enthalpy  $\rightarrow$  (H)  $\rightarrow$  Enthalpy of a system is defined as

$$H = U + PV \text{ --- (42)}$$

Diff. eqn. (42) we get

$$dH = dU + PdV + VdP$$

But

$$dU = TdS - PdV$$

$$\therefore dH = Tds - PdV + PdV + VdP$$

$$\text{or } dH = Tds + VdP \quad \text{--- (43)}$$

Diff. H Partially w.r.t. S and P we get

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{and} \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{--- (44)}$$

Since dH is a perfect differential, so

$$\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P}\right) = \frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S}\right)$$

Using eqn. (44) we get

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \quad \text{--- (45)}$$

This is the second Maxwell's thermodynamical relation

#### 4. Gibb's Function or Gibb's free Energy (G)

Gibb's function is defined as

$$G = H - TS$$

$$G = U + PV - TS \quad [ \because H = U + PV ] \quad \text{--- (46)}$$

Diff. eqn (46) we get

$$dG = dU + PdV + VdP - Tds - SdT$$

$$\text{But } dU = Tds - PdV$$

$$\therefore dG = VdP - SdT \quad \text{--- (47)}$$

Taking Partial differentiation of G w.r.t. P and T, we get

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{--- (48)}$$

Since dG is a perfect differential, so

$$\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right)$$

Using eqn. (48), we get

$$\left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial S}{\partial P}\right)_T \quad \text{--- (49)}$$

This is fourth Maxwell's thermodynamical relation.

## Applications of Maxwell's Relations :-

Variation of Internal Energy with Volume :- Consider the first Tds equation. That is

$$dU = Tds - PdV \quad \text{--- (50)}$$

Divide by dV to obtain

$$\frac{dU}{dV} = T \frac{ds}{dV} - P \quad \text{--- (51)}$$

This eqn. gives the change in internal energy U with volume for any substance during infinitesimal process.

Suppose the process occurs at constant temperature. The eqn. (51) takes the form:

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial s}{\partial V}\right)_T - P \quad \text{--- (52)}$$

Using the Maxwell relation

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

it becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P \quad \text{--- (53)}$$

This eqn. gives the variation of internal energy with volume during an isothermal process.

(a) For perfect gas :- The eqn. of state for one mole of perfect gas is

$$PV = RT$$

$$P = \frac{RT}{V} \quad \text{--- (54)}$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad \text{--- (55)}$$

Substituting this result in eqn. (53) we obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V} - P \quad \text{--- (56)}$$

Using eqn. (54) it becomes

$$\left(\frac{\partial U}{\partial V}\right)_T = P - P = 0 \quad \text{--- (57)}$$

Thus the internal energy of a perfect gas is independent of its volume.

Integrating eqn. (57) we obtain

$$U = U(T) \quad \text{--- (58)}$$

This eqn. shows that the internal energy of a perfect gas is only a function of temperature.

(b) For Vander Waal Gas  $\rightarrow$  The eqn. of state for one mole of gas is

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

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{--- (59)}$$

Differentiate this eqn. partially w.r.t.  $T$  keeping volume constant. This gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \quad \text{--- (60)}$$

Substitute this result in eqn. (53) to obtain

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V-b} - P \quad \text{--- (61)}$$

Using eqn. (59) it takes the form

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

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} \quad \text{--- (62)}$$

Since  $a$  is positive, the internal energy of a Vander Waal gas (i.e. actual gas) increases during isothermal expansion.

Integrating eqn. (62) we obtain

$$U = -\frac{a}{V} + f(T) \quad \text{--- (63)}$$

where  $f(T)$  is some function of temperature. Eqn. (63) shows that the internal energy of a real gas depends on both its volume and temperature.

Variation of  $C_v$  with volume  $\rightarrow$  The specific heat at constant volume is defined as

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_V \quad \text{--- (64)}$$

$$\text{But } dQ = T ds$$

$$\text{Thus } C_v = T \left(\frac{\partial S}{\partial T}\right)_V \quad \text{--- (65)}$$

Differentiate both sides w.r.t. volume keeping temperature constant. This gives

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

$$\left(\frac{\partial C_v}{\partial V}\right)_T = T \frac{\partial^2 S}{\partial V \partial T} \quad \text{--- (66)}$$

Now consider the Maxwell's relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad \text{--- (67)}$$

Diff. it partially w.r.t.  $T$  keeping volume constant. This gives

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

$$\left(\frac{\partial^2 S}{\partial T \partial V}\right) = \left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad \text{--- (68)}$$

Substitute this result in eqn. (67) to obtain

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \quad \text{--- (69)}$$

This eqn. gives the variation of  $C_V$  with volume during isothermal process

(a) For a perfect gas  $\rightarrow$  The eqn. of state for one mole of perfect gas is

$$PV = RT$$

$$P = \frac{RT}{V} \quad \text{--- (70)}$$

Diff. this eqn. w.r.t.  $T$  keeping  $V$  constant. This gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad \text{--- (71)}$$

Diff. it again w.r.t.  $T$  keeping  $V$  constant. We obtain

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0 \quad \text{--- (72)}$$

Substitute this value in eqn. (69) to obtain

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0 \quad \text{--- (73)}$$

This eqn. shows that  $C_V$  does not change with volume during adiabatic expansion or compression of perfect gas.

(b) For a Vander Waal gas: The eqn. of state for one mole of actual gas is

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

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \text{--- (74)}$$

Diff. this eqn. twice w.r.t. temperature keeping volume constant.

This gives

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

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0 \quad \text{--- (15)}$$

Eqn. (14) takes the form

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0 \quad \text{--- (16)}$$

Thus there is no change in  $C_V$  with volume during isothermal expansion or compression for a van der Waal gas also

Variation of  $C_p$  with Pressure:- The molar specific heat at constant pressure is defined as

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_P \quad \text{--- (17)}$$

But

$$dQ = T ds$$

Thus, <sup>above</sup> eqn. (17) takes the form

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_P \quad \text{--- (17)}$$

Diff. both sides w.r.t.  $P$  keeping temperature constant. This gives

$$\left(\frac{\partial C_p}{\partial P}\right)_T = \frac{\partial}{\partial P} \left[ T \left(\frac{\partial S}{\partial T}\right)_P \right]_T$$

$$\left(\frac{\partial C_p}{\partial P}\right)_T = T \frac{\partial^2 S}{\partial P \partial T} \quad \text{--- (18)}$$

Now consider the Maxwell relation

$$\left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial S}{\partial P}\right)_T \quad \text{--- (19)}$$

Diff. both sides w.r.t.  $T$  keeping  $P$  constant. This gives

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

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = - \frac{\partial^2 S}{\partial T \partial P} \quad \text{--- (20)}$$

Substitute this value in eqn. (18) to obtain

$$\left(\frac{\partial C_p}{\partial P}\right)_T = - T \left(\frac{\partial^2 V}{\partial T^2}\right)_P \quad \text{--- (21)}$$

This eqn. gives the variation of  $C_p$  with pressure during isothermal change.

(a) For a perfect gas:- The eqn. of state for one mole of perfect gas is

$$PV = RT$$

$$V = \frac{RT}{P} \quad \text{--- (22)}$$

Diff. this eqn. twice w.r.t.  $T$  keeping pressure constant. This gives

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \quad (83)$$

$$\therefore \left(\frac{\partial^2 V}{\partial T^2}\right)_P = 0 \quad (83)$$

Substitute this value in eqn. (81) to obtain

$$\left(\frac{\partial C_p}{\partial P}\right)_T = 0 \quad (84)$$

Thus  $C_p$  does not vary with pressure for a perfect gas at constant temperature.

General Relation between  $C_p$  and  $C_v$  : The molar specific heat at constant pressure is given as

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_P \quad (85)$$

Let us assume that entropy  $S$  is a function of temperature  $T$  and volume  $V$ . That is

$$S = S(T, V) \quad (86)$$

The total differential of  $S$  is

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \quad (87)$$

Therefore

$$\frac{dS}{dT} = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \frac{dV}{dT} \quad (88)$$

$$\text{or} \quad \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (89)$$

Substitute this value in eqn. (70) to obtain

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_V + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (90)$$

Using eqn. (65) it becomes

$$C_p = C_v + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (91)$$

$$C_p - C_v = T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (92)$$

Using Maxwell Relation

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

in eqn. (92) we obtain

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad (93)$$

(a) For a perfect Gas: The eqn. of state for one mole of perfect gas

$$PV = RT$$

$$P = \frac{RT}{V} \quad \text{--- (94)}$$

Diff. this eqn. partially w.r.t.  $T$  keeping volume constant. This gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad \text{--- (95)}$$

Thus eqn. (93) becomes

$$C_p - C_v = \frac{RT}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (96)}$$

Eqn. (94) may be written as

$$V = \frac{RT}{P} \quad \text{--- (97)}$$

Diff. it w.r.t.  $T$  keeping  $P$  constant we obtain

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \quad \text{--- (98)}$$

Substitute this result in eqn. (96) to obtain

$$C_p - C_v = \frac{RT}{V} \frac{R}{P} = \frac{R^2 T}{PV}$$

$$C_p - C_v = \frac{R^2 T}{RT}$$

$$C_p - C_v = R \quad \text{--- (99)}$$

This is well known result for a perfect gas

(b) For Vander Waal Gas: This eqn. of state for 1 mole of actual gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{--- (100)}$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \quad \text{--- (101)}$$

Differentiate this eqn. partially w.r.t.  $T$  keeping volume constant. This gives

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b} \quad \text{--- (102)}$$

Now differentiate eqn. (100) w.r.t.  $T$  keeping pressure constant. This gives

$$\left(P + \frac{a}{V^2}\right) \left(\frac{\partial V}{\partial T}\right)_P + (V - b) \left[0 - \frac{2a}{V^3} \left(\frac{\partial V}{\partial T}\right)_P\right] = R$$

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

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

$$\left(\frac{\partial V}{\partial T}\right)_P \left[ P - \frac{a}{V^2} + \frac{2ab}{V^3} \right] = R$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left( P - \frac{a}{V^2} + \frac{2ab}{V^3} \right)} \quad \text{--- (103)}$$

Using eqn. (102) and (103) in eqn (93) we obtain

$$C_p - C_v = \frac{TR}{V-b} \frac{R}{\left( P - \frac{a}{V^2} + \frac{2ab}{V^3} \right)}$$

$$C_p - C_v = \frac{R^2 T}{(V-b) \left( P - \frac{a}{V^2} + \frac{2ab}{V^3} \right)} \quad \text{--- (104)}$$

Using eqn. (101) it takes the form

$$C_p - C_v = \frac{R^2 T}{(V-b) \left( \frac{RT}{V-b} - \frac{2a}{V^2} + \frac{2ab}{V^3} \right)} \quad \text{--- (105)}$$

This gives the general expression for  $C_p - C_v$  for real gases

Special Cases : Case 1  $\rightarrow$  The Vander Waal gas becomes identical with a perfect gas for  $a \rightarrow 0, b \rightarrow 0$ . Thus taking the limit of right hand side when both  $a$  and  $b$  approach zero, we obtain

$$C_p - C_v = \frac{R^2 T}{V \left( \frac{RT}{V} - 0 + 0 \right)} = R$$

This result is identical with eqn. (99).

Case 2  $\rightarrow$  Since  $a$  and  $b$  are small quantities, the term  $\frac{2ab}{V^3}$  can be neglected in comparison to other terms. Thus eqn. (105) takes the form

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

$$C_p - C_v = \frac{R^2 T V^2}{R T V^2 - 2a(V-b)} = \frac{R^2 T V^2}{R T V^2 - 2aV + 2ab} \quad \text{--- (106)}$$

Neglecting term  $2ab$  it becomes

$$C_p - C_v = \frac{R^2 T V^2}{R T V^2 - 2aV} = \frac{R^2 T V^2}{R T V^2 \left( 1 - \frac{2a}{R T V} \right)}$$

$$C_p - C_v = R \left( 1 - \frac{2a}{R T V} \right)^{-1} \quad \text{--- (107)}$$

Expanding by Binomial and retaining first order term it becomes

$$C_p - C_v = R \left( 1 + \frac{2a}{R T V} \right) \quad \text{--- (108)}$$