

Maxwell's Thermodynamical equations & some important deductions

The state of a homogeneous system is completely determined by any pair of thermodynamical variables P, V, T, U and S . Of these five thermodynamic variables only two are independent, the rest being automatically fixed by the values of these two. Among these five variables certain relations exist which are known as Maxwell's thermodynamic relations. Let us deduce these as follows -

According to the first law and 2nd law of thermodynamics, we have respectively

$$dQ = dU + Pdv$$

-and $dQ = Tds$

From these two, we obtain

$$dU + Pdv = T \cdot ds$$

$$\text{or } dU = T \cdot ds - P \cdot dv \quad \text{--- ①}$$

We now choose two independent variables x and y which determine the state of a body of a given mass. It means, any thermodynamic variable will be a function of x and y

$$\text{Let } \left. \begin{aligned} U &= f(x, y) \\ S &= f(x, y) \\ V &= f(x, y) \end{aligned} \right\}$$

Then, we have (according usual rules of Calculus differentials)

$$dU = \left(\frac{\partial U}{\partial x} \right)_y dx + \left(\frac{\partial U}{\partial y} \right)_x dy$$

$$dS = \left(\frac{\partial S}{\partial x} \right)_y dx + \left(\frac{\partial S}{\partial y} \right)_x dy$$

$$\text{and } dV = \left(\frac{\partial V}{\partial x} \right)_y dx + \left(\frac{\partial V}{\partial y} \right)_x dy$$

Putting these values of du , ds and dv in eqn we have

$$\frac{\partial U}{\partial x} dx + \frac{\partial U}{\partial y} dy = T \left(\frac{\partial S}{\partial x} dx + \frac{\partial S}{\partial y} dy \right) - P \left(\frac{\partial V}{\partial x} dx + \frac{\partial V}{\partial y} dy \right)$$

Equating the Co-efficients of dx and dy on both sides, we obtain

$$\frac{\partial U}{\partial x} = T \frac{\partial S}{\partial x} - P \frac{\partial V}{\partial x} \quad \text{--- (II)}$$

$$\text{and } \frac{\partial U}{\partial y} = T \frac{\partial S}{\partial y} - P \frac{\partial V}{\partial y} \quad \text{--- (III)}$$

Now differentiating (II) w.r. to y and (III) w.r. to x , we get

$$\frac{\partial^2 U}{\partial y \partial x} = \frac{\partial T}{\partial y} \frac{\partial S}{\partial x} + T \frac{\partial^2 S}{\partial y \partial x} - \frac{\partial P}{\partial y} \frac{\partial V}{\partial x} - P \frac{\partial^2 V}{\partial y \partial x}$$

$$\text{and } \frac{\partial^2 U}{\partial x \partial y} = \frac{\partial T}{\partial x} \frac{\partial S}{\partial y} + T \frac{\partial^2 S}{\partial x \partial y} - \frac{\partial P}{\partial x} \frac{\partial V}{\partial y} - P \frac{\partial^2 V}{\partial x \partial y}$$

$$\text{But } \frac{\partial^2 U}{\partial y \partial x} = \frac{\partial^2 U}{\partial x \partial y}, \quad \frac{\partial^2 S}{\partial y \partial x} = \frac{\partial^2 S}{\partial x \partial y} \quad \text{and} \quad \frac{\partial^2 V}{\partial y \partial x} = \frac{\partial^2 V}{\partial x \partial y}$$

because ∂U , ∂S and ∂V are all perfect differentials. Hence we obtain

$$\boxed{\frac{\partial T}{\partial y} \frac{\partial S}{\partial x} - \frac{\partial P}{\partial y} \frac{\partial V}{\partial x} = \frac{\partial T}{\partial x} \frac{\partial S}{\partial y} - \frac{\partial P}{\partial x} \frac{\partial V}{\partial y}} \quad \text{--- (IV)}$$

This is the most general form of Maxwell's thermodynamic relations. Let us now substitute any pair of variables P, V, T and S for the independent variables x and y and different Maxwell's equations are obtained.

Let us put $x = T$ and $y = V$ in eqn (IV)

$$\text{Then, } \frac{\partial T}{\partial x} = 1 \text{ and } \frac{\partial V}{\partial y} = 1; \quad \frac{\partial T}{\partial y} = 0 \text{ and } \frac{\partial V}{\partial x} = 0$$

Since T and V are independent. Hence we have

$$\boxed{\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V} \quad \text{--- (V) 1st Maxwell's eqn}$$

Let us now put $x=T$ and $y=P$ Equation (IV) then reduces to

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (VI) This is the Maxwell's 2nd. eqn.}$$

If we put $x=S$ and $y=V$ in eqn (IV), we get

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{--- (VII) 3rd Maxwell's equation.}$$

Again on putting $x=S$ and $y=P$ in eqn (IV) we get

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{--- (VIII) 4th Maxwell's equation.}$$

The above relations (V), (VI), (VII) and (VIII) are known as four Maxwell's thermodynamic relations. Besides these, there are two more relations of mathematical interests only.

If we put $x=P$ and $y=V$ in eqn (IV) we get

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1 \quad \text{--- (IX)}$$

This is the 5th relation.

Similarly, by putting $x=T$ and $y=S$ in eqn: (IV), we get the 6th relation as

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 \quad \text{--- (X)}$$

Two Tds equations

There are two Tds equations derived as follows —

Let the entropy s of a thermodynamic system be a function of temp. T and volume V

$$\text{i.e. } S = f(T, V)$$

Since ds is a Perfect differential, hence we can write

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

Multiplying both sides by T , we have

$$T \cdot ds = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV. \quad \text{--- (I)}$$

Now $T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = C_v$ according to definition, the specific heat at Const. volume.

Also $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ from Maxwell's relation

Putting these values in equation (I), we obtain

$$T ds = C_v dT + T \left(\frac{\partial P}{\partial T}\right)_V dV. \quad \text{--- (XI)}$$

This is called the first T.ds equation

2nd Tds equation - If the entropy s of a thermodynamic system is a function of T and P

$$\text{i.e. } S = f(T, P)$$

Since ds is a Perfect differential, hence we can write

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

Multiplying by T ,

$$T \cdot ds = T \left(\frac{\partial S}{\partial T}\right)_P dT + T \left(\frac{\partial S}{\partial P}\right)_T dP \quad \text{--- II.}$$

Now $T \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P = C_p = \text{specific heat at Const Pressure}$

and $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ from Maxwell's 2nd relation

Hence Putting these values in (II), we have

$$T \cdot ds = C_p dT - T \left(\frac{\partial v}{\partial T} \right)_P dP$$

This is known as 2nd T.ds equation.

Clapeyron's equation

Maxwell's fourth thermodynamical equation

" $\left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial p}{\partial T} \right)_v$ can be applied to the equilibrium between two states of the same substance.

Multiplying both sides by T , we get.

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

$$\text{or } \left(\frac{\partial Q}{\partial v} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_v$$

Which means that the latent heat of isothermal expansion is equal to the product of absolute temp and the rate of increase of pressure with temp at const. volume. Thus, if a body changes its phase at T° and absorbs latent heat L_p and the specific volumes in the first and second phases are v_1 and v_2 then the above eqn yields

$$\frac{L}{v_2 - v_1} = T \left(\frac{\partial p}{\partial T} \right)_v$$

When we apply this equation to change of phase, the various thermodynamic quantities refer to a mixture of the liquid and vapour in equilibrium. For such a case, it is evident that

$$\left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial p}{\partial T} \right)_{\text{sat}}$$

Since the pressure is saturation pressure and is consequently independent of V , being only a function of T . Hence

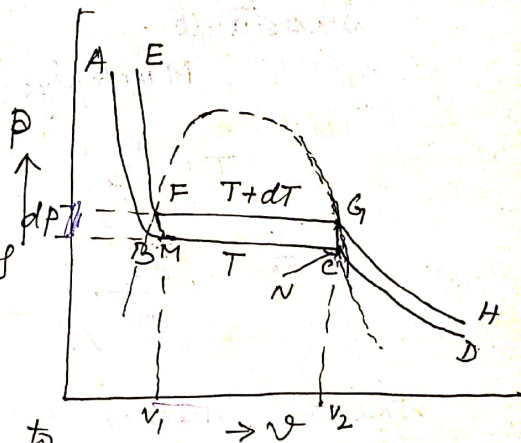
$$\left(\frac{\partial P}{\partial T}\right)_{\text{sat}} = \frac{L}{T(V_2 - V_1)}$$

This is Clapeyron's equation.

Alternative rigorous proof has been given as below.

Clapeyron deduced the above relation with the help of Carnot cycle.

Let ABCD and EFGH be two consecutive isotherms at temps. T and $T+dT$. From F & G draw two adiabatics meeting the 2nd isothermal at M and N. Now let us suppose



a unit mass of substance to be taken through the reversible Carnot cycle FGNM, by allowing it to expand isothermally along FG, adiabatically along GN and compressing it along NM isothermally and then adiabatically along MF. The substance at F is in liquid state and at G is in the form of vapour. The amount of heat taken during this cycle is therefore $L+dL$ at temp $T+dT$. Therefore the work done during the cycle is by the 2nd law

$$(L+dL)\left(1 - \frac{T}{T+dT}\right) = \frac{LdT}{T} \text{ to the first order.}$$

Again the work done during the cycle = area of parallelogram FGNM = $(V_2 - V_1)dP$.

$$\therefore \frac{LdT}{T} = (V_2 - V_1)dP$$

$$\therefore \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \text{ which is the Clapeyron's equation.}$$

Ehrenfest Phase transition

We have already dealt with Clapeyron's equation which is the equation for first order phase transition. Recent investigations particularly with liquid helium, have brought to light some phenomenon where during phase transition no latent heat is evolved and there is no change in volume. This led Ehrenfest to examine the nature of these phase transition of higher order. We define a second order phase transition as that takes place at constant temp and pressure with no change of entropy and volume.

In other words, phase changes of the 2nd order are such that there is no discontinuity but merely a continuous change in the first-order derivatives of the Gibbs's function when substances pass from one phase to another phase.

The characteristic of 2nd-order phase transition has been shown diagrammatically & mathematically it can be written as follows

$$g_1 - g_2 = 0$$

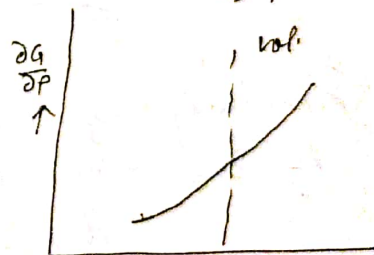
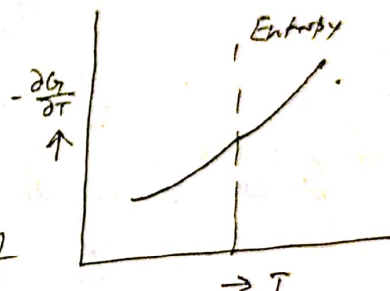
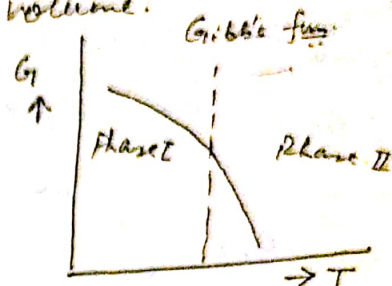
where g_1 and g_2 denote thermodynamic potentials of the saturated liquid and the saturated vapour per unit mass.

$$-\left(\frac{\partial g_2}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial T}\right)_P = S_2 - S_1 = 0$$

$$\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T = v_2 - v_1 = 0$$

Further since $\left(\frac{C_p}{T}\right) = \left(\frac{\partial S}{\partial T}\right)_P = \frac{\partial}{\partial T} \left[-\left(\frac{\partial g}{\partial T}\right)_P \right]_P = -\left(\frac{\partial^2 g}{\partial T^2}\right)_P$

$$k v = -\left(\frac{\partial v}{\partial P}\right)_T = -\frac{\partial}{\partial P} \left[\left(\frac{\partial g}{\partial P}\right)_T \right]_T = -\left(\frac{\partial^2 g}{\partial P^2}\right)_T$$



$$\alpha v = \left(\frac{\partial v}{\partial T} \right)_P = \frac{\partial}{\partial T} \left[\left(\frac{\partial g}{\partial P} \right)_T \right]_P = \frac{\partial^2 g}{\partial T \partial P}$$

where k is isothermal compressibility and α the volume Co-efficient of expansion; we have

$$\left(\frac{\partial^2 g_2}{\partial T^2} \right)_P - \left(\frac{\partial^2 g_1}{\partial T^2} \right)_P = \frac{C_{p2}}{T} - \frac{C_{p1}}{T}$$

$$\left(\frac{\partial^2 g_2}{\partial P^2} \right)_T - \left(\frac{\partial^2 g_1}{\partial P^2} \right)_T = v(k_2 - k_1)$$

$$\frac{\partial^2 g_2}{\partial T \partial P} - \frac{\partial^2 g_1}{\partial T \partial P} = v(\alpha_2 - \alpha_1)$$

if we assume that $S_1 = S_2$ (at T, P)

and $S_1 + dS_1 = S_2 + dS_2$ (at $T+dT, P+dP$)

we have $dS_1 = dS_2$

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

$$\therefore \frac{C_{p1}}{T} dT - v\alpha_1 dP = \frac{C_{p2}}{T} dT - v\alpha_2 dP$$

Since v is the same in both the Phases, Hence

$$\frac{dP}{dT} = \frac{C_{p2} - C_{p1}}{T v (\alpha_2 - \alpha_1)} \quad \text{--- (I)}$$

Similarly if we assume $v_1 = v_2$ for the change of 2nd order we get as before

$$dv_1 = dv_2$$

$$\text{Since } dv = \left(\frac{\partial v}{\partial T} \right)_P dT + \left(\frac{\partial v}{\partial P} \right)_T dP$$

we have

$$v\alpha_1 dT - v k_1 dP = v\alpha_2 dT - v k_2 dP$$

$$\text{or } \frac{dP}{dT} = \frac{\alpha_2 - \alpha_1}{k_2 - k_1} \quad \text{--- (II)}$$

Equations (I) & (II) are called Ehrenfest Phase transition equations.

Ex. Transition of liquid helium I to helium II.

Transition at the Curie Point of a ferromagnetic to Paramagnetic.
 . . . et .

Enthalpy (H) : — (Or Total Heat)

It is the Property of a thermodynamical System given by the mathematical expression

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

This is also known as the total heat.

Differentiating it,

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= Tds - PdV + PdV + VdP \quad \left(\text{Since } dU = Tds - PdV \right) \\ &= Tds + VdP \quad \text{--- (II)} \end{aligned}$$

Since H is a function of entropy and Pressure, hence Partially differentiating it

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

All the quantities in the case of enthalpy are perfect differential, hence H is a perfect differential

$$\text{So } \frac{d}{dP} \left(\frac{\partial H}{\partial S} \right)_P = \frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P} \right)_S$$

$$\text{Or } \left(\frac{\partial T}{\partial P} \right)_V = \left(\frac{\partial V}{\partial S} \right)_P \quad \text{which is Maxwell's thermodynamical relation}$$

Helmholtz's function (F)

From 1st and 2nd Law of thermodynamics

$$dU = Tds - dW$$

If the system is maintained at const. temp, then $Tds = d(TS)$

$$\therefore dU = d(TS) - dW$$

$$\text{or } -dW = d(U - TS)$$

$$\text{or } dF = -dW$$

where $F = U - TS$ is known as Helmholtz free energy or Helmholtz work function

$$\begin{aligned}
 \text{Now } dF &= d(U - TS) \\
 &= dU - Tds - s dT \\
 &= Tds - PdV - Tds - s dT \\
 &\quad (\because dU = Tds - PdV) \\
 &= -PdV - s dT
 \end{aligned}$$

Here free energy is a function of vol. and temp.
 We have on Partial Differentiation,

$$\left(\frac{\partial F}{\partial T}\right)_V = -s$$

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

Since dF is a Perfect differential

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

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

This is also the Maxwell's thermodynamical relation.

Gibb's function (G)

From Enthalpy relation, we have

$$dH = Tds + vdp$$

$$\text{For isothermal Process } Tds = d(Ts)$$

$$\text{For isobaric Process } dp = 0$$

Hence, if the Process is both isothermal and isobaric, then $dH = d(Ts)$

$$\text{or } d(H - Ts) = 0$$

$$\text{or } dG = 0$$

$$\begin{aligned}
 \text{The function } G &= H - TS \\
 &= U + PV - TS
 \end{aligned}$$

is known as thermodynamic Potential at Constant Pressure or Gibb's function.

Differentiating the above eqn. we get

$$\begin{aligned}
 dG &= dU + PdV + vdp - Tds - sdt \\
 &= \cancel{Tds} - PdV + PdV + vdp - \cancel{Tds} - sdt \\
 &= vdp - sdt
 \end{aligned}$$

In this case G is a function of Pressure and temp. Hence on partially differentiating it

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

In this case G is a Perfect differential
Hence

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

$$\text{or} \quad \left(\frac{\partial v}{\partial T} \right)_P = - \left(\frac{\partial s}{\partial P} \right)_T$$

This is also a Maxwell's thermodynamical relation.