Dr. L. K. Mishra
Deptt of chemistry

FOR Deg II Chem Hons Paper III &
Deg II Sub Courses

The free energy changes with variation of temperature and Pressure may now be considered.

We know that $G = H - TS$

and $H = E + PV$

$\therefore G = E + PV - TS$ —— (1)

upon differentiating equation (1) we get

$dG = dE + Pdv + Vdp - Tds - SdT$ —(2)

According to the first Law of Thermodynamics

$$\delta q = dE + \delta w$$

If the work done δw is only due to expansion then $\delta q = dE + Pdv$

Now for a reversible process

$$ds = \frac{\delta q}{T}$$

$\therefore dq = Tds = dE + Pdv$ —(3)

Putting the value of Tds in eq(2)

$dG = dE + Pdv + Vdp - dE - Pdv - SdT$

or $\boxed{dG = Vdp - SdT}$ —(4)

This equation gives change of free energy when a system undergoes reversibly, a change of Pressure & Temperature.

If Pressure remains Constant

i.e $dp = 0$

$\therefore dG = -s\,dT$

or $\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S}$ —— (5)

On the other hand if temperature remains constant i.e $dT = 0$

Then $dG = V\,dp$

$\boxed{\text{or } \left(\frac{\partial G}{\partial P}\right)_T = V}$ —— (6)

Let the free energy of a system be G_1 in the state 1 and G_2 be the final state. When an appreciable change in pressure has taken place at constant temperature. Then free energy change ~~ΔG~~ ΔG is given by

$$\Delta G = G_2 - G_1 = \int_{P_1}^{P_2} V\,dp$$

where P_1 and P_2 are the initial and final pressure respectively

$$\Delta G = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\boxed{\Delta G = RT \log \frac{P_2}{P_1}} = \boxed{RT \log \frac{V_1}{V_2}}$$

where V_1 and V_2 are initial and final volume.

Free energy change in Reversible & Irreversible reaction

As we know that change of entropy for a given change of state is a definite quantity, independent of the fact whether, the change is brough about reversibly or Irreversibly.

For small change it is given by the equation —

$$ds = \frac{\delta q}{T} = \frac{dE + PdV}{T}$$

only if the change is brought about reversibly

Let us suppose now that the small change of state is brought about irreversibly. The work done by the system will now be less than before. Therefore, the heat absorbed will also be less (1st Law Thermodynam But ds will have the same value.

$$ds > \frac{\delta q}{T} > \frac{dE + PdV}{T}$$

Thus We may Write

$$Tds = dE + PdV$$ (For reversible reaction)

$$Tds > dE + PdV$$ (For Irreversible)

We know that

$dG = dE + Pdv + vdp - Tds - sdT$

We have $dG = vdp - sdT$ (For Reversibl

or $dG < vdp - sdT$ (For Irreversible process)

If the change takes place at constant Pressure and Temperatur

Hence $(\partial G)_{T,P} = 0$ (For reversible)

$(\partial G)_{T,P} < 0$ (For Irreversible)

For a big change these equation may be written as

$(\Delta G)_{T,P} = 0$ (For reversible process)

$(\Delta G)_{T,P} < 0$ (For Irreversible Process)

This gives a criterion for distinguishing between a reversible and Irreversible process. Free energy during a reversible process is zero. Free energy during spontaneous process has a negative value.