

Gibbs-Helmholtz Equation

By Gibbs Energy: $G = H - TS$

Enthalpy $\rightarrow \Delta H = \Delta E + p\Delta V$ (at const pressure)

Entropy $\rightarrow T\Delta S = \Delta q$ (at const temp)

$$\therefore G = E + pV - TS$$
$$\Rightarrow \Delta G = \Delta E + (p\Delta V + V\Delta p) - (T\Delta S + S\Delta T)$$

By 1st law: $dE = dq - pdV$

By 2nd law: $dq = TdS$

$$\therefore dG = dE + pdV + Vdp - TdS - SdT$$
$$= dq - pdV + pdV + Vdp - dq - SdT$$

$$\therefore dG = Vdp - SdT$$

But At constant pressure ($dp = 0$)

$$\therefore dG = -SdT$$
$$\Rightarrow \frac{dG}{dT} = -S$$

for any 2 states of system: $\left. \begin{aligned} dG_1 &= -S_1 dT \\ dG_2 &= -S_2 dT \end{aligned} \right\}$

$$dG_2 - dG_1 = -S_2 dT - (-S_1 dT)$$
$$\Rightarrow d\Delta G = -(S_2 - S_1) dT$$
$$= -\Delta S dT$$

$$\Rightarrow \boxed{\frac{d\Delta G}{dT} = -\Delta S}$$

By Gibbs energy:- $\Delta G = \Delta H - T\Delta S$ (const temp)

$$\Rightarrow -\Delta S = \frac{\Delta G - \Delta H}{T}$$

But ~~ΔS~~ $\Delta S = \frac{d\Delta G}{dT}$ \rightarrow at const pressure

$$\therefore \frac{d\Delta G}{dT} = \frac{\Delta G - \Delta H}{T}$$

$$\Rightarrow T \left(\frac{d\Delta G}{dT} \right)_P = \Delta G - \Delta H$$

$$\Rightarrow \Delta G = \Delta H + T \left(\frac{d\Delta G}{dT} \right)_P$$

This is Gibbs-Helmholtz eqⁿ in terms of

- Gibbs' free energy
- Enthalpy