

❖ **Gibbs free energy**

❖ **Variation of Gibbs free energy with temperature and pressure**

❖ **Gibbs-Helmholtz Equation**

Qn: Calculate the entropy change when 5 moles of an ideal gas expand reversibly from a volume of 8 dm³ to 80 dm³ at a temperature of 27 °C?

Ans: The entropy change, $\Delta S = nR \ln (V_2/V_1)$
 $= 5 \times 8.314 \times 2.303 \log (80/8)$
 $= 5 \times 8.314 \times 2.303 \log 10$
 $= 95.736 \text{ J K}^{-1}$

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \quad (\text{for reversible process})$$

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0 \quad (\text{for irreversible process})$$

Gibbs's Free Energy (G)

- Tells us about the spontaneity of a process.
- The Gibbs free energy is the maximum amount of non-expansion work that can be extracted from a closed system which can be attained only in a completely reversible process.
- ❖ The Gibbs free energy change at temperature T is expressed as,

$$\Delta G = \Delta H - T\Delta S$$

a negative ΔG = spontaneous

a positive ΔG = nonspontaneous

The free energy function G is given as

$$G = H - TS$$

As H and S depended only upon the state of a system, G also depend upon the state of the system
Only

If G_1 , H_1 and S_1 represent the thermodynamic functions of a system in the initial state

And G_2 , H_2 and S_2 in the final state at constant temperature,

$$\begin{aligned}\text{Then } G_2 - G_1 &= (H_2 - TS_2) - (H_1 - TS_1) \\ &= (H_2 - H_1) - T(S_2 - S_1)\end{aligned}$$

$$\text{Or, } \Delta G = \Delta H - T\Delta S$$

$$= \Delta U + P\Delta V - T\Delta S$$

$$= \Delta U + P\Delta V - q_{\text{rev}}$$

$$\Delta G = (\Delta U - q_{\text{rev}}) + P\Delta V$$

$$\Delta G = -w + P\Delta V \quad [\text{as } \Delta U = q - w \text{ (1}^{\text{st}} \text{ law of thermodynamics)}]$$

$$\text{Or, } -\Delta G = w - P\Delta V$$

Here, $P\Delta V$ is the work done due to the expansion of the gas against constant external pressure P

Hence, $-\Delta G$ gives the maximum work (net work) obtainable from a system other than that due to change of volume at constant temperature and pressure

Variation of Gibbs's Free Energy Change (ΔG) with temperature and pressure

The free energy function G is given as

$$G = H - TS$$
$$= U + PV - TS$$

Upon differentiation, $dG = dU + P dV + VdP - T dS - S dT$ (1)

For an infinitesimal small change,

$$dq = dU - dw$$
$$= dU + P dV \text{(2)}$$

For a reversible process, $dS = dq/T$

$$\text{Or, } dq = T dS \text{(3)}$$

From Eq. 2 and 3, $dq = dU + P dV = T dS$

Now Eq. 1 can be written as, $dG = (dU + P dV) + VdP - T dS - S dT$

$$= T \cancel{dS} + VdP - T \cancel{dS} - S dT$$

$$\text{or, } dG = VdP - S dT \text{(4)}$$

This equation gives the change of free energy when a system undergoes reversibly a change of pressure as well as temperature

Gibbs's Free Energy Change (ΔG) at constant temperature

$$dG = VdP - S dT$$

If temperature remains constant, then $dG = VdP$ (as $dT = 0$)

$$\text{Or, } (\partial G / \partial P)_T = V$$

Let the free energy of a system in the initial state be G_1
and in the final state be G_2 at constant temperature

The free energy change, ΔG of the system can be given by,

$$\begin{aligned}\Delta G &= \int_{P_1}^{P_2} V dP \\ &= \int_{P_1}^{P_2} (RT/P) dP \\ &= RT \int_{P_1}^{P_2} (dP/P)\end{aligned}$$

$$\Delta G = RT \ln (P_2/P_1) = RT \ln (V_1/V_2)$$

Where V_1 and V_2 are initial and final volumes, respectively.

$$\text{For } n \text{ moles of the gas, } \Delta G = nRT \ln (P_2/P_1) = nRT \ln (V_1/V_2) \dots\dots\dots (5)$$

Gibbs' Free Energy change (ΔG)

$$\Delta G = \Delta H - T\Delta S$$

-	-	+	energetically favorable entropically favorable always spontaneous
+	+	-	energetically unfavorable entropically unfavorable never spontaneous
+/-	+	+	energetically unfavorable entropically favorable spontaneous at high T
+/-	-	-	energetically favorable entropically unfavorable spontaneous at low T

Gibbs-Helmholtz Equation

Let the free energy of a system in the initial state at temperature T be G_1 .

Suppose the temperature rises to $T+dT$ and the free energy at this temperature be G_1+dG_1

$$\text{Thus, } dG_1 = -S_1 dT \dots\dots\dots(1)$$

If the free energy of the system in its final state is G_2 at the temperature T and G_2+dG_2 at Temperature $T+dT$, then $dG_2 = -S_2 dT \dots\dots\dots(2)$

Subtracting Eq. 1 from Eq. 2, we have

$$dG_2 - dG_1 = - (S_2 - S_1) dT$$

$$\text{Or, } d(\Delta G) = - \Delta S dT$$

$$\text{As the pressure is constant, we can write } (\partial(\Delta G)/\partial T)_p = - \Delta S \dots\dots\dots(3)$$

We know that $\Delta G = \Delta H - T\Delta S$

Hence, $\Delta G - \Delta H = -T\Delta S$

Or, $(\Delta G - \Delta H)/T = -\Delta S \dots\dots\dots(4)$

From Eqs. 3 and 4, $(\Delta G - \Delta H)/T = (\partial(\Delta G)/\partial T)_p$

or, $\Delta G - \Delta H = T (\partial(\Delta G)/\partial T)_p$

or, $\Delta G = \Delta H + T (\partial(\Delta G)/\partial T)_p \dots\dots\dots(5)$

This Eq. 5 is known as the **Gibbs-Helmholtz equation**.

This equation is applicable to all processes occurring at **constant pressure**.

- ❖ This equation is useful for calculating the **heat change ΔH for a process taking place at constant pressure** if the values of free energy changes at two different temperatures are known

Ex: The free energy change accompanying a given process is -85.77 kJ at 25 °C and -83.68 kJ at 35 °C. Calculate the change in enthalpy (ΔH) for the process at 30 °C?

Ans: ΔG at 25 °C = -85.77 kJ and at 35 °C = -83.68 kJ

$$(\partial(\Delta G)/\partial T)_p = [(-83.68) - (-85.77)] / (308 - 298) \text{ kJ K}^{-1}$$

$$= 2.09 / 10 \text{ kJ K}^{-1}$$

$$= 0.209 \text{ kJ K}^{-1}$$

$$\Delta G \text{ at } 30^\circ\text{C} = - (85.77 + 83.68) / 2 \text{ kJ}$$

$$= - 84.725 \text{ kJ}$$

$$\text{Now, } \Delta G = \Delta H + T (\partial(\Delta G)/\partial T)_p$$

$$\text{or, } - 84.725 \text{ kJ} = \Delta H + 303 \text{ K} (0.209 \text{ kJ K}^{-1})$$

$$= \Delta H + 63.327 \text{ kJ}$$

$$\text{or, } \Delta H = (- 84.725 - 63.327) \text{ kJ}$$

$$\text{or, } \Delta H = - 148.052 \text{ kJ}$$