

Gibbs energy and Gibbs energy change and

Spontaneity: Gibbs energy of a system is defined as the maximum amount of energy available to a system during a process that can be converted into useful work.

In other words, it is a thermodynamic quantity which is a measure of capacity of a system to do useful work. It is denoted by symbol G and is given by

$$G = H - TS$$

where H is the enthalpy of the system, S is its entropy and T is the absolute temperature. Gibbs energy is also called as Gibbs function. It is extensive property and a state function. The change in Gibbs energy of the system may be expressed as.

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

This equation is called Gibbs Helmholtz equation and is very useful in predicting the spontaneity of a process.

Units of ΔG : kJ mol^{-1} OR J mol^{-1} .

Spontaneity of a chemical change: we know that for spontaneous reaction $\Delta S_{\text{total}} = +ve$
so, $\Delta G = -ve$ for spontaneous chemical changes.

Thus spontaneity of a chemical change can be predicted either by

- i) $T \Delta S_{\text{system}} = +ve$ or
- ii) $\Delta G = -ve$.

By calculating ΔH and $T \Delta S$ and hence ΔG , we can easily predict whether reaction is spontaneous or not.

- 1. When energy and entropy factors are favourable i.e. ΔH is (-ve) and $T \Delta S$ is (+ve), then ΔG must be (-ve).

$$\Delta G = (-) - (+) = -ve$$

Thus ΔG is (-ve) for a spontaneous process.

- 2. If both the tendencies oppose, i.e., ΔH is (+ve) and $T \Delta S$ is (-ve), then ΔG is (+ve).

$$i.e. \Delta G = (+) - (-) = +ve$$

Thus ΔG is positive for a non-spontaneous process.

- 3. If both the tendency are equal and opposite, the $\Delta G = 0$. At this stage the process does not proceed in either direction and the reaction is said to be in equilibrium state.

In short, we can say

- i) If ΔG is negative, the process is spontaneous.
- ii) If ΔG is zero, the process is in equilibrium state. There is no net reaction in either direction.
- iii) If ΔG is positive, the process does not occur in the forward direction. It may however, go in the reverse direction.

Conditions for spontaneous processes i.e. ΔG negative.

S.No.	ΔH	$T \Delta S$	Magnitude of the tendency
1.	(-)(Favourable)	(+) Favourable	Any magnitude
2.	(-)(Favourable)	(-) Unfavourable	$\Delta H > T \Delta S$
3.	(+)(Unfavourable)	(+) favourable	$T \Delta S > \Delta H$

Standard Gibbs energy change: The standard Gibbs energy change is defined as the Gibbs energy change for a process in which the reactants in their standard states are converted to the products in their standard state.

$$\Delta G = \sum \Delta_f \Delta G^\circ_{(product)} - \sum \Delta_f G^\circ_{(reactants)}$$

$$= \left[\begin{array}{l} \text{Sum of the standard} \\ \text{Gibbs energy of} \\ \text{formation of products} \end{array} \right] - \left[\begin{array}{l} \text{Sum of the standard} \\ \text{Gibbs energy of the} \\ \text{formation of reactants} \end{array} \right]$$

Q. Calculate the standard Gibbs free energy change from the free energies of formation & data for the

following reaction. $C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(g)$

Soln. Given. that $\Delta_f G^\circ [C_6H_6(l)] = 172.8 \text{ kJ mol}^{-1}$

$$\Delta_f G^\circ [CO_2(g)] = -394.4 \text{ kJ mol}^{-1}$$

$$\Delta_f G^\circ [O_2(g)] = 0$$

$$\Delta_f G^\circ [H_2O(g)] = -228.6 \text{ kJ mol}^{-1}$$

Solution: $\Delta G^\circ = \sum \Delta_f G^\circ (\text{Product}) - \sum \Delta_f G^\circ (\text{Reactant})$

$$\Delta G^\circ = [6 \Delta_f G^\circ [CO_2(g)] + 3 \Delta_f G^\circ [H_2O(g)] - \Delta_f G^\circ [C_6H_6(l)] + \frac{15}{2} \Delta_f G^\circ [O_2(g)]]$$

$$\Delta G^\circ = 6 \times (-394.4) + 3 \times (-228.6) - \{172.8 + 0\}$$

$$\boxed{\Delta G^\circ = -3225 \text{ kJ mol}^{-1}}$$

Absolute Entropy and Third law of thermodynamics

According to third law of thermodynamics at absolute zero the entropy of a perfectly crystalline substance is taken as zero.