

Class \Rightarrow B.Sc. Hons. Part - II
 Subject \Rightarrow Chemistry
 Chapter \Rightarrow Second law of Thermodynamics

Topic \Rightarrow Criteria for spontaneity of a process.

Name \Rightarrow Dr. Amarendra Kumar
 Deptt. of Chemistry
 Jain College, Arq.

Criteria for spontaneity of a process

In second law of thermodynamics, the following generalisations were derived

- If $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$,
 the process is irreversible i.e. it is spontaneous.
- If $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$,
 the process is reversible i.e. the system is in equilibrium.

The above two results are combined and represented as

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0 \quad \text{--- (1)}$$

Where the sign greater than i.e. an irreversible process or spontaneous process and the sign equal to for a reversible process.

for an infinitesimal change, the above criteria is written as

$$dS_{\text{system}} + dS_{\text{surroundings}} \geq 0 \quad \text{--- (2)}$$

Where the sign, $>$ for irreversible process and the sign, $=$ for the reversible process.

If the surroundings lose heat δQ reversibly and isothermally at the temperature T (which may be absorbed by the system reversibly or irreversibly),

Then

$$\text{surroundings} = \frac{\partial U}{\partial T}$$

According to the first law of thermodynamics
 $\Delta H = \Delta U + \Delta V$

Putting this value in eqn ②, we get

$$\text{surroundings} = \frac{\partial U + \Delta V}{T}$$

Substituting this value in eqn ③, we get

$$\text{system} = \frac{\partial U + \Delta V}{T} > 0$$

$$\text{or } Tds - \Delta U - \Delta V > 0$$

$$\text{or } Tds \geq \Delta U + \Delta V$$

where ds stands for the entropy change of the system without the subscript system.

Equation ④ is the basic eqn which leads to a no. of criteria for predicting the spontaneity of a process.

In this equation the sign $=$ stands for the reversible process and the sign $>$ for the irreversible process.

From eqn ④ the various criteria may be deduced as under

(i) In terms of entropy change of the system \Rightarrow

If the internal energy and the volume of the system are kept constant

$$dU=0 \text{ and } dV=0$$

Then from eqn ④, we have

$$(Tds)_{U,V} \geq 0$$

$$\text{or } (ds)_{U,V} \geq 0$$

where the sign $=$ is for the reversible process and the sign $>$ for the irreversible process. The subscripts U and V indicate that these properties remain constant.

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Page No.:						YOUNA
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(3)

(2) In terms of Internal energy change of the system \Rightarrow
If the entropy and volume of the system are kept constant.

$$ds = 0 \text{ and } dv = 0$$

Then eqn. (6) becomes

$$0 \geq (du)_{s,v}$$

$$\text{or } (du)_{s,v} \leq 0 \quad (8)$$

where the sign $=$ stands for the reversible process and the sign $<$ for the irreversible process.

This implies that if a process under constant entropy and volume is accompanied by a decrease of internal energy, the process is irreversible; if no change of internal energy takes place, the process is reversible.

(3) In terms of enthalpy change of the system \Rightarrow

$$H = U + PV$$

complete differentiation of this eqn. gives

$$dH = du + pdv + vdp$$

$$\text{or } du + pdv = dH - vdp$$

Putting this value in eqn. (6), we get

$$Tds \geq dH - vdp$$

If entropy and pressure of the system are kept constant,

$$ds = 0 \text{ and } dp = 0, \text{ so that}$$

$$0 \geq (dH)_{s,p}$$

$$\text{or } (dH)_{s,p} \leq 0 \quad (9)$$

where the sign $=$ refers to the reversible process and the sign $<$ refers to the irreversible process.

(4) In terms of change in work function of the System \Rightarrow

$$A = U - TS$$

Complete differentiation of this eqn. gives

$$dA = du - Tds - SdT$$

④

$$\text{or, } Tds = dU - SdT - dA$$

Putting this value in eqn ⑥, we get

$$dU - SdT - dA \geq dU + Pdv$$

$$\text{or } - SdT - dA \geq Pdv$$

$$\text{or } SdT + dA \leq - Pdv$$

If temperature and volume of the system are kept constant then

$$dT = 0 \text{ and } dv = 0, \text{ so}$$

$$(dA)_{T,V} \leq 0$$

where sign = is for the reversible process and the sign < for the irreversible process.

(5) In terms of free energy change of the system \Rightarrow

$$G = H - TS$$

$$\text{further } H = U + PV$$

$$\therefore G = U + PV - TS$$

complete differentiation of this equation gives

$$dG = dU + Pdv + vdp - Tds - SdT$$

$$\text{or, } dU + Pdv = dG - vdp + Tds + SdT$$

Putting this value in eqn ⑥, we get

$$Tds \geq dG - vdp + Tds + SdT$$

$$\text{or, } 0 \geq dG - vdp + SdT$$

$$\text{or, } dG - vdp + SdT \leq 0$$

If pressure and temperature of the system are kept constant, then

$$dp = 0 \text{ and } dT = 0, \text{ so that}$$

$$(dG)_{PT} \leq 0$$

where the sign = for the reversible process and sign < for the irreversible process.

The criterion in terms of free energy change is most important because most of the processes take place at constant temperature and pressure.

(i) If $(dG)_{PT} < 0$, the process is irreversible i.e. it is feasible.

(5)

- (ii) If $(dG)_{P,T} = 0$ the process is reversible i.e. the system is in equilibrium.
- (iii) If $(dG)_{P,T} > 0$, the process does not occur i.e. it is not feasible.

\rightarrow Summary