Thermodynamics

TOPICS COVERED

- Free Energy Functions: Gibb's and Helmholz Energy
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  - Gibb's Free Energy
- The effect of temperature and pressure on Free energy
- Spontaneity criteria of ΔG

Free Energy Functions: Gibb's and Helmholz Energy

Free Energy

- A measure of a system's ability to do work.
- Formula of free energy is q-TS at constant pressure and formula of Helmholz Energy is q-TS at constant volume, where q is quantity of heat absorbed by a system, TS is unavailable heat for doing useful work.

Helmholz Energy (A)

- It is Extensive property
- It is a state function
- Formula of Helmholz Energy is E-TS ----------(1)

Helmholz Energy

$A_1 = E_1 - T_1S_1$

$A_2 = E_2 - T_2S_2$

Substrate whole equation at constant T

$\Delta A = \Delta E - T \Delta S$

$\Delta A = \Delta E - q_{rev}$ ……(2) $(\Delta S = \frac{q_{rev}}{T}, T \Delta S = q_{rev})$

But by the Ist law of thermodynamics

$\Delta E = q + w$

$w_{rev} = \Delta E - q_{rev}$

$-w_{max} = \Delta E - q_{rev}$ ……(3) (when work is done by the system)

Comparing eq 2 to 3

$\Delta A = -w_{max}$ or $-\Delta A = w_{max}$

- Decrease in work function A (i.e. $-\Delta A$) gives max. work that can be done by the system during the giving change.

Gibb's Free Energy

- It is Extensive property
- It is a state function
- Formula of Gibb's Free Energy is G= H-TS --------(4)

$G_1 = H_1 - T_1S_1$

$G_2 = H_2 - T_2S_2$

at constant T

$\Delta G = \Delta H - T \Delta S$ ……(5)

$\Delta G = \Delta E + P\Delta V - T\Delta S$ $(\Delta H = \Delta E + P\Delta V)$

We know that

$\Delta E - T\Delta S = \Delta A$ ……(6)

Put the values

$\Delta G = \Delta A + P\Delta V$

Since $\Delta A = -w_{max}$

So, $\Delta G = -w_{max} + P\Delta V$

$-\Delta G = w_{max} - P \Delta V$ (Net work)

- Negative sign of ΔG indicates the spontaneous process.
- Negative sign of ΔG indicates the non spontaneous process.
- If the value of ΔG is zero then the condition is in equilibrium

The effect of temperature and pressure on Free energy

Considering the equation (4)

$G = H - TS$

And also $H = U + PV$ ……(7)

Substituting equation (7) in equation (2) we get:

$G = U + PV - TS$ ……(8)

Differentiating the above equation

$dG = dU + PdV + VdP – TdS – SdT$……(9)

For infinitesimal small change, the first law equation can be written as:

$dq = dU – dw$ ……(10)

As $– dw = PdV$ substituting this in equation (10)

$dq = dU + PdV$ ……(11)

Making the use of equation

$dS = dq/T$ or $TdS = dq = dU + PdV$ ……(12)

Combining equation (9) and (12)

$dG = VdP - SdT$ ……(13)

The above equation gives the change in free energy on variation of temperature and pressure. If pressure of the system kept constant then dP = 0,thus equation (13) becomes:

$dG = -SdT$ ……(14)

Rearranging the above equation:

$(\delta G / \delta T)_P = - S$ ……(15)

Similarly if temperature of the system is kept constant then, dT = 0, Thus equation (13) becomes:

$$dG = VdP$$

$$(\delta G / \delta P)_T = V$$

Spontaneity criteria of ΔG

$$\Delta S_{total} = \Delta S_{system} + \Delta s_{surrounding}$$

We know that

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

$$\Delta S_{total} = \Delta S + \frac{q_{surrounding}}{T_{surrounding}}$$

$$q_{surrounding} = -q_{system} = -\Delta H_{system}$$

$$\Delta S_{total} = \Delta S - \frac{\Delta H}{T}$$

Multiply whole equation with T

$$T\Delta S_{total} = T\Delta S - \Delta H$$

$$T\Delta S_{total} = -\Delta G \quad \text{or} \quad \Delta G = -T\Delta S_{total}$$

So, for any spontaneous system the value of ΔG is negative and for any non spontaneous system the value of ΔG is positive.

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