

Entropy change in an isothermal Expansion of ideal gas.

Isothermal expansion of an ideal gas carried out reversibly, there will be no change in internal energy

i.e. $\Delta U = 0$ and hence from the 1st law equation
(i.e. $\Delta U = q + w$)

$$q_{rev} = -w \quad \text{--- (1)}$$

In such a case, the workdone in the expansion of n moles of a gas from volume V_1 to V_2 at constant temperature T is given by

$$-w = nRT \ln \frac{V_2}{V_1} \quad \text{--- (2)}$$

From equation (1) and (2),

$$q_{rev} = -w = nRT \ln \frac{V_2}{V_1}$$

Dividing by T both side, $\frac{q_{rev}}{T} = \frac{nRT}{T} \ln \frac{V_2}{V_1}$

$$\text{or } \Delta S = \frac{q_{rev}}{T} = \frac{nRT}{T} \ln \frac{V_2}{V_1}$$

$$= \frac{q_{rev}}{T} = nR \ln \frac{V_2}{V_1}$$

$$\text{i.e. } \Delta S = nR \ln \frac{V_2}{V_1} \quad \text{--- (3)}$$

eqn (3) defines the entropy change in an isothermal expansion of ideal gas.

Entropy Change in Reversible and Irreversible Process.

Let us consider isothermal expansion of an ideal gas in vacuum i.e. irreversible process, there is no opposing force. So, $W = 0$ and T is constant so $\Delta U = 0$ (from the 1st law), $Q = 0$ i.e. no heat supplied or removed from surrounding.

In this condition volume is increased from V_1 to V_2 at constant temperature then entropy change for 1 mole of gas is given by

$$\Delta S = R \ln \frac{V_2}{V_1} \quad \text{--- (1)}$$

So the total increase in entropy of the system and its surrounding during irreversible isothermal expansion $= R \ln \frac{V_2}{V_1} + 0$.

$$= R \ln \frac{V_2}{V_1}$$

Since $V_2 > V_1$, it is obvious that irreversible isothermal expansion of a gas is accomplished by the increase in the entropy of the system and its surrounding considered together.

Now consider isothermal reversible expansion of ideal gas from volume V_1 to V_2 at temperature T .

The gas does some external work $W = -P\Delta V$

and equivalent amount of heat (Q_{rev}) is absorbed by the system from surrounding at temperature T .

Hence increase in entropy of the system is Q_{rev}/T and also heat loss by surrounding is Q_{rev} Hence decrease in the entropy of surrounding is Q_{rev}/T .

Providing + sign for increase in entropy and -ve sign for decrease in entropy is given as

Net change in entropy of the system and its surrounding

$$= \frac{Q_{rev}}{T} - \frac{Q_{rev}}{T} = 0$$

Now it is clear that a thermodynamically irreversible process is always accompanied by increase in entropy of the system and its surrounding taken together.

While in reversible thermodynamic process the entropy of the system and its surrounding taken together remains unchanged so, we can write

$$\begin{aligned} (\Delta S_{sys} + \Delta S_{sur}) &= 0 && \text{(For reversible process)} \\ \& \quad (\Delta S_{sys} + \Delta S_{sur}) &> 0 && \text{(For irreversible process)} \\ \text{or } (\Delta S_{sys} + \Delta S_{sur}) &\geq 0 \end{aligned}$$

Clausius summed up 1st and 2nd Law of thermodynamics as the energy of the universe remains constant, the entropy of the universe tend towards a maximum.

Work function and free energy function.

The work function A and free energy function G is defined by the following equations.

$$A = U - TS \quad \text{--- (1)}$$

$$G = H - TS \quad \text{--- (2)}$$

The work function A and free energy function G depends upon the state of the system only.

At constant temperature T , the A_1, U_1 and S_1 are the functions in one state and A_2, U_2 and S_2 are the functions in another state.

$$\text{then, } A_1 = U_1 - TS_1 \quad \text{--- (3)}$$

$$A_2 = U_2 - TS_2 \quad \text{--- (4)}$$

From eqⁿ (3) and (4).

$$A_2 - A_1 = U_2 - U_1 - T(S_2 - S_1)$$

$$\Delta A = \Delta U - T\Delta S \quad \text{--- (5)}$$

Let the change is brought about reversibly at constant temperature T and heat absorbed is equal to q_{rev} .

$$\text{we know, } \Delta S = \frac{q_{rev}}{T}$$

$$\therefore q_{rev} = T\Delta S$$

On substituting the value of $T\Delta S$ in equation (5)

$$\Delta A = \Delta U - q_{rev} \quad \text{--- (6)}$$

$$\text{From 1st law, } \Delta U = q + w$$

$$\text{i.e. } w_{rev} = \Delta U - q_{rev} \quad \text{--- (7)}$$

If work is done by the system, it is negative

$$\text{so, } -w_{rev} = \Delta U - q_{rev} \quad \text{--- (8)}$$

From equation (6) and (8) we have

$$-\Delta A = w_{rev}$$

Since process is reversible, w represents the maximum work. so, it is clear that decrease in work function A (i.e. $-\Delta A$) gives the maximum work.

Work function A is also referred as Helmholtz Free Energy or Helmholtz Function.

Gibbs Free Energy

The free energy function is named in honour of American Physicist J. W. Gibbs and represented by symbol G and eqn is given as, $G = H - TS$
If G_1, H_1 and S_1 represents the thermodynamic function in initial state and G_2, H_2 and S_2 are in final state at constant temperature T .

$$\text{then, } G_1 = H_1 - TS_1$$

$$G_2 = H_2 - TS_2$$

$$(G_2 - G_1) = (H_2 - H_1) - T(S_2 - S_1)$$

$$\text{or, } \Delta G = \Delta H - T\Delta S \quad \text{———— (1)}$$

But, at constant pressure, we know

$$\Delta H = \Delta U + P\Delta V$$

On substituting the value ΔH in eqn (1) we have

$$\Delta G = \Delta U + P\Delta V - T\Delta S \quad \text{———— (2)}$$

we know

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

On substituting the above value in eqn (2)

$$\Delta G = \Delta A + P\Delta V \quad \text{———— (3)}$$

$$\text{and } \Delta A = -W$$

$$\therefore \Delta G = -W + P\Delta V \quad \text{———— (4)}$$

Here $-\Delta G$ gives the maximum work.

The work other than that due to change of volume is called Network.

$$\text{Thus, Network} = W - P\Delta V = -\Delta G \quad \text{———— (5)}$$

The quantity G is called Gibbs's function or Gibbs-free energy or Free energy.

And $-\Delta G$ is a measurement of the decrease in free energy.

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Variation of free energy change with Temperature and Pressure

We know, $G = H - TS$
and $H = U + PV$

On putting the value of H,

$$G = U + PV - TS \quad \text{--- (1)}$$

On differentiating the above equation

$$dG = dU + PdV + VdP - Tds - SdT \quad \text{--- (2)}$$

From 1st law, for infinitesimal, 1st law equation may be written as

$$dq = du - dw \quad \text{--- (3)}$$

If work is done due to expansion, then

$$-dw = PdV \quad \text{--- (4)}$$

$$\therefore dq = du + PdV \quad \text{--- (5)}$$

For a reversible process,

$$ds = \frac{dq_{rev}}{T}$$

$$\text{or } Tds = dq_{rev}$$

$$\text{and } dq_{rev} = du + PdV$$

$$\therefore Tds = du + PdV \quad \text{--- (6)}$$

On putting the value of Tds in equation (2) we have,

$$dG = dU + PdV + VdP - (dU + PdV) - SdT$$

$$\text{or } dG = \cancel{dU} + PdV + VdP - \cancel{dU} - PdV - SdT$$

$$dG = VdP - SdT \quad \text{--- (7)}$$

$$\left. \begin{array}{l} \text{If pressure is const. } dP = 0, \therefore \Delta G = -SdT \\ \text{or } \left(\frac{\partial G}{\partial T}\right)_P = -S \end{array} \right\} \quad \text{--- (8)}$$

If temperature remains constant $dT = 0$

$$\therefore dG = VdP - SdT$$

$$\therefore dG = VdP \quad \text{--- (9)}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = V$$

If G_1 and G_2 are initial and final free energy of the system at constant temperature and an appreciable change in pressure has taken place

On integrating eq (9)

$$dG = V dP$$

$$\Delta G = RT \int \frac{dP}{P}$$

$$\Delta G = RT \ln \frac{P_2}{P_1}$$

$$\therefore \Delta G = RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_2}{V_1} \quad \text{--- (10)}$$

Where V_1 and V_2 are initial and final volume.

For n mole of Gas

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_2}{V_1} \quad \text{--- (11)}$$

$$\left[\text{For 1 mole } PV = RT \right. \\ \left. V = RT/P \right]$$

Gibbs - Helmholtz Equation

Let us consider that in initial state G_1 is free energy at temperature T , if temp. rise $T+dT$, where dT is infinitesimal small, then free energy $G_1 + dG_1$ at temp. $T+dT$.

Now G_2 is free energy in final state at temperature T and $G_2 + dG_2$ is free energy at temp. $T+dT$.

If pressure is constant along all procedure.

We know eqⁿ $dG = Vdp - SdT$

If pressure is constant, $dp = 0$

$$\therefore dG = -SdT$$

$$\therefore dG_1 = -S_1 dT \quad \text{--- (1)}$$

$$dG_2 = -S_2 dT \quad \text{--- (2)}$$

Where S_1 and S_2 are entropies of the system in initial and final state.

From eqⁿ (1) and (2) we have

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

$$d\Delta G = -\Delta S dT$$

The pressure is constant,

$$\left(\frac{\partial(\Delta G)}{\partial T} \right)_P = -\Delta S \quad \text{--- (3)}$$

$$\therefore G = H - TS$$

We know,

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

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

$$\text{or } -\Delta S = \frac{\Delta G - \Delta H}{T} \quad \text{--- (4)}$$

From Equation (3) and (4)

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

$$\text{or } \Delta G - \Delta H = T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P$$

$$\text{or } \Delta G = \Delta H + T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P \quad \text{--- (5)}$$

This equation (5) is known as Gibbs-Helmholtz equation.

For reaction at constant volume, the corresponding equation will be,

$$\Delta A = \Delta U + T \left(\frac{\partial(\Delta U)}{\partial T} \right)_V$$

Entropy of a mixture of ideal gas

We know for one mole of an ideal gas the entropy equation is as follows.

$$ds = C_v \ln \frac{dT}{T} + R \frac{dv}{v} \quad \text{--- (1)}$$

On integrating the above equation assuming C_v constant of ideal gas

$$\int ds = C_v \ln \int \frac{dT}{T} + R \int \frac{dv}{v} \quad \text{--- (2)}$$

$$s = C_v \ln T + R \ln v + s_0 \quad \text{(where } s_0 \text{ is integration constant)}$$

$\therefore C_p - C_v = R$ and $v = \frac{RT}{P}$, we have

$$s = C_p \ln T - R \ln P + R \ln R + s_0 \quad \text{--- (3)}$$

$$\text{or, } s = C_p \ln T - R \ln P + s'_0 \quad \text{--- (4)}$$

s'_0 is (where $s'_0 = R \ln R + s_0$) another constant.

Entropy of a system consisting of a mixture of gases is the sum of individual entropies of the constituents at pressure or concentration existing in the mixture.

If n_1, n_2, n_3, \dots etc are various gases in mixture and P_1, P_2, P_3, \dots etc are their partial pressures. The entropy of mixture is given by

$$S = n_1 (C_p \ln T - R \ln P_1 + s'_0) + n_2 (C_p \ln T - R \ln P_2 + s'_0) + n_3 (C_p \ln T - R \ln P_3 + s'_0) + n_4 (C_p \ln T - R \ln P_4 + s'_0) + \dots$$

$$S = \sum n_i (C_p \ln T - R \ln P_i + s'_0) \quad \text{--- (5)}$$

The Partial Pressure (P) of an ideal gas is given by

$$P = x P \quad \left[\begin{array}{l} \text{where } x = \text{mole fraction of} \\ \text{particular gas} \\ \text{and } P = \text{total pressure} \end{array} \right]$$

If $P = x P$, now eqn (5) becomes.

$$S = \sum n_i (C_p \ln T - R \ln P - R \ln x + s'_0) \quad \text{--- (6)}$$

Entropy of mixing - It is difference of entropy of mixture of gas and the sum of the entropies of separate gases at pressure P .

$$\Delta S_{\text{mix}} = \sum n_i (C_p \ln T - R \ln P - R \ln x + s'_0) - \sum n_i (C_p \ln T - R \ln P + s'_0) \quad \text{--- (7)}$$

$$\Delta S_{\text{mix}} = -R \sum n_i \ln x = -R (n_1 \ln x_1 + n_2 \ln x_2 + \dots) \quad \text{--- (8)}$$

$$= R \sum n_i \ln x_i \quad \text{--- (9)}$$

where $n_i = \text{no. of moles}$, $x_i = \text{mole fraction of each constituent of the mixture}$

If $n = n_1 + n_2 + n_3 + \dots$ --- (10)

eqn (9), on dividing both side by n , we have

$$1 = \frac{n_1}{n} + \frac{n_2}{n} + \frac{n_3}{n} + \dots \quad \text{--- (11)}$$

for 1 mole of gas mixture ($\sum n_i = \sum x_i$), then entropy of mixture is given by

$$\Delta S_{\text{mix}} = -R \sum x_i \ln x_i \quad \text{--- (12)}$$

Since x_i is a fraction, the entropy of mixing is always positive.