Unit-I US06CCHE23

Entropy and third law of thermodynamics.

* Topics :

- Third law of thermodynamics
- Molecular basis of entropy
- Translational entropy
- Rotational entropy
- Vibrational entropy
- Molecular basis of third law.
- Trouton's rule
- Free-energy
- Standard free-energy of formation
- Free-energy and pressure
- Free-energy and the equilibrium constant.
- Free-energy and ~~p~~ temperature
- Free-energy function
- Equilibria and Distributions
- Fugacity
- Numericals

* Reference Book :-

Physical chemistry by Gordan M. Barrow
5th edition.

* Third law of thermodynamics :-

→ Statement :- "The entropy of perfect crystals at all pure elements and compounds is zero at the absolute zero of temperature $^\circ K$."

The entropy of a substance at any temperature can be calculated from its entropy at another temperature is known.

$$\therefore ds = Cp \cdot \frac{dT}{T}$$

Integrating the equation, limits are $^\circ K$ and $T^\circ K$

$$\therefore \int_0^T ds = \int_0^T Cp \; dT/T$$

Higher limit - lower limit

$$\therefore S_T - S_0 = \int_0^T Cp \cdot dT/T \quad (\text{or}) \quad \int_0^T Cp \, d\ln T$$

According to third law of thermodynamics, $S_0 = 0$

$$\therefore S_T = \int_0^T Cp \cdot dT/T$$

where S_T is known as absolute entropy at temperature T.

* Molecular Basis of Entropy :-

The entropy is a property of a chemical system. It increases when an isolated system moves towards the equilibrium state. This change towards equilibrium is accompained by an increase in probability, thus energy is related with probability.

Consider a chemical reaction between A and B. Assuming that, concentration of B is favoured at equilibrium $A \rightleftharpoons B$, then at equilibrium concentration of B is more and of A is less, therefore available quantum states of B are more and A is less. The ways of distributing atoms in these levels are more in B and less in A, therefore the probability of B is more and A is less at equilibrium.

Conclusion :- A substance (state) for which the molecule possess more number of available states also possess higher entropy.

The relation between entropy (S) and the probability (the number of arrangements) can be given as,

$$\boxed{\therefore S = K \ln W} \quad \text{——} ①$$

where,

W = the no. of different molecular level arrangements of the system.

K = Boltzmann's constant $(\because K = R/N)$

This is the relation between a macroscopic property and a microscopic property at microscopic levels.

For Avagadro's number of 'N' molecules, the probability can be represented as,

$$\because W = \left(g_1^{N_1}\, g_2^{N_2}\, g_3^{N_3} \text{----}\right) \frac{1}{N_1!\,N_2!\,N_3!\,\ldots} \quad \text{——} ②$$

where,

$g_1, g_2, g_3, \ldots$ are the multiplicities of $1^{st}, 2^{nd}, 3^{rd}, \ldots$ levels and $N_1, N_2, N_3, \ldots$ are the populations of the $1^{st}, 2^{nd}, 3^{rd}, \ldots$ levels.

Taking logarithm of eq^n ②, we get

$$\therefore \ln W = N_1 \ln g_1 + N_2 \ln g_2 + \ldots - [\ln N_1! + \ln N_2! + \ldots]$$

$$\therefore \ln W = \Sigma N_i \ln g_i - \Sigma \ln N_i! \quad \text{———} ③$$

Applying stirling approximation,

$$[\ln x! \cong x \ln x - x]$$

$$\therefore \ln N_i! \cong N_i \ln N_i - N_i \quad \text{———} ④$$

Substitute the value of eq^n ④ in eq^n ③, we get,

$$\therefore \ln W = \Sigma N_i \ln g_i - \Sigma (N_i \ln N_i - N_i) \quad \text{———} ⑤$$

$$\therefore \ln W = \Sigma N_i \ln g_i - \Sigma N_i \ln N_i + \Sigma N_i$$

$$\therefore \ln W = \Sigma N_i [1 + \ln g_i - \ln N_i]$$

$$\therefore \ln W = \Sigma N_i [1 + \ln g_i / N_i] \quad \text{———} ⑥$$

For Avagadro's number of particles,

$$\therefore \frac{N_i}{g_i} = \frac{N}{q} e^{-(E_i - E_0)/KT} \quad \text{———} ⑦$$

where q is the partition function

The reciprocal at eq^n ⑦ is,

$$\therefore \frac{g_i}{N_i} = \frac{q}{N} e^{[E_i - E_0]/KT} \quad \text{———} ⑧$$

Take the logarithium of eqⁿ ⑧, we get ·

$$\therefore \ln \frac{g_i}{N_i} = \ln \frac{q}{N} + \frac{E_i - E_0}{KT} \quad \text{———} \quad ⑨$$

Substitute the value of eqⁿ ⑨ in eqⁿ ⑥, we get,

$$\therefore \ln W = \Sigma N_i \left[1 + \ln \frac{q}{N} + \frac{E_i - E_0}{KT}\right] \text{———} ⑩$$

Substitute the value of eqⁿ ⑩ in eqⁿ ①, we get·

$$\therefore S = K \ln W$$

$$\therefore S = K\left[\Sigma N_i \left(1 + \ln \frac{q}{N} + \frac{E_i - E_0}{KT}\right)\right]$$

$$\therefore S = K\left[\Sigma N_i + \Sigma N_i \ln \frac{q}{N} + \Sigma N_i \frac{E_i - E_0}{KT}\right]$$

$$\therefore S = K\Sigma N_i + K\Sigma N_i \ln \frac{q}{N} + \frac{K}{\cancel{K}T} \Sigma N_i (E_i - E_0).$$

$$\therefore S = K\Sigma N_i \left[1 + \ln q/N\right] + \frac{1}{T} \Sigma N_i (E_i - E_0).$$

$$\therefore S = K\mathcal{N}\left[1 + \ln q/N\right] + \frac{1}{T} \Sigma N_i (E_i - E_0)$$

(∵ $\Sigma N_i = \mathcal{N}$ - the total no. of molecules)

$$\therefore S = \frac{1}{T} \Sigma N_i (E_i - E_0) + K\mathcal{N}\left[1 + \ln \frac{q}{N}\right] \text{———} ⑪$$

The summation of the energy term is the thermal energy of the system. Hence,

$$\frac{1}{T} \Sigma N_i (E_i - E_0) = \frac{U_{Thermal}}{T} = \frac{U - U_0}{T}$$

and $K\mathcal{N} = R$

Equation ⑪ becomes,

$$\therefore S = \frac{U - U_0}{T} + R\left[1 + \ln q/_N\right]$$

$$\therefore S = \frac{U - U_0}{T} + R \ln \frac{q}{N} + R \quad \text{——} \quad ⑫$$

when the standard states of 1 bar is,

$$\therefore S = \frac{U - U_0^\circ}{T} + R \ln \frac{q^\circ}{N} + R \quad \text{——} \quad ⑬$$

From this, the standard entropy of the system can be calculated from the knowledge of thermal energies and the Boltzman distribution.

Limitations :-

(1) Expression derived for gaseous system only, not for solids (or) liquids.

(2) When almost all molecules are distributed in lower level, the Boltzman's low does not work. The entropy calculations are not satisfactory.

* Entropy and Degree of Freedom :-

For many gases, at not too high temperature for thermodynamic calculations of molecular motions and degree of freedom, we consider translational, vibrational and rotational motion.

For some molecules at lower temperature and for all molecules at elevated temperatures, electronic states other than single ground state must be considered.

The energy of the molecules of a gas is given by,

$$\therefore U - U_0 = (U-U_0)_{trans.} + (U-U_0)_{vib.} + (U-U_0)_{rot.} + (U-U_0)_{ele.} \quad \text{——} (1).$$

$$\therefore q = q_{trans.} \times q_{rot} \times q_{vib.} \times q_{ele.} \quad \text{——} (2).$$

but

$$S = \frac{U - U_0}{T} + R \ln \frac{q}{N} + R \quad \text{——} (3).$$

Substitute the value of $U - U_0$ and q in eq^n ③, we get,

$$\therefore S = \frac{(U-U_0)_{trans}}{T} + \frac{R \ln q_{trans}}{N} + R$$

$$+ \frac{(U-U_0)_{rot}}{T} + R \ln q_{rot}.$$

$$+ \frac{(U-U_0)_{vib.}}{T} + R \ln q_{vib}.$$

$$+ \frac{(U-U_0)_{ele}}{T} + R \ln q_{ele}.$$

The assignment of the N term and the additional R term to the translational component produces a translational entropy component with the form of the expression for the entropy obtained

The entropy of any ideal gas by adding the terms of,

$$\therefore S = S_{trans.} + S_{rot.} + S_{vib.} + S_{ele.}$$

* Translational Entropy :-

The entropy of translational motion of the molecule can be calculated by the use of translational energy and partition function.

Translational entropy is given by,

$$\therefore S_{trans.} = \frac{(U-U_0)_{trans.}}{T} + R \ln \frac{q_{trans.}}{N} + R \quad \text{——— (1)}$$

The translational energy of one mole of gas is $3/2 RT$ and partition function, $q_{trans.}$ is equal to $\left(\frac{2\pi m k T}{h^2}\right)^{3/2} V$.

Eq^n(1) becomes,

$$\therefore S_{trans.} = \frac{3/2\, RT}{T} + R \ln \left(\frac{2\pi m k T}{h^2}\right)^{3/2} \frac{V}{N} + R$$

$$\therefore S_{trans.} = \frac{3}{2} R + R \ln \left(\frac{2\pi m k T}{h^2}\right)^{3/2} \frac{V}{N} + R$$

$$\therefore S_{trans.} = R \left[3/2 + \ln \left(\frac{2\pi m k T}{h^2}\right)^{3/2} \frac{V}{N} \right] \quad \text{——— (2)}$$

Numerically,

(1) Standard conditions of 1-bar pressure, the standard molar entropy as,

$$\therefore S^0_{trans.} (J/K\ mole) = 76.57 + 12.47 M + 20.79 \ln T$$

(1 bar, M in Kg/mole)

(2) At 25°c, this expression becomes,

$$\therefore S_{trans} (J/K\ mole) = 195.00 + 12.47 \ln M$$

$\left(1 \text{ bar, at } 25°c, M \text{ in } \frac{Kg}{mole}\right)$

* Rotational Entropy :-

The entropy due to the rotational motion of the molecules of a gas can be calculated.

There are two types of rotational motion of the molecules of a gas.

(1) Linear Molecule :-

The rotational motion (energy) of a gas for linear molecule is,

$$\therefore E_{rot.} = J(J+1)\frac{\hbar^2}{2I} \quad \text{where } \hbar = \frac{h}{2\pi}$$

For rotational motion,

$$\therefore S_{rot.} = \frac{(U-U_0)_{rot.}}{T} + R\ln q_{rot.} \text{ ——— } (1)$$

For linear molecule, $(U-U_0)_{rot.} = RT$ —— (2)

The partition function for rotational linear molecule is,

$$\therefore q_{rot.} = \frac{2IKT}{\sigma\hbar^2}$$

$$\therefore q_{rot.} = \frac{2IKT}{\sigma}\cdot\frac{4\pi^2}{h^2} \qquad (\because \hbar = h/2\pi)$$

$$\therefore q_{rot.} = \frac{8\pi^2 IKT}{\sigma h^2} \text{ ——— } (3)$$

Substitute the value of eq^n ② and eq^n ③ in eq^n ①, we get,

$$\therefore S_{rot} = \frac{RT}{T} + R\ln\frac{8\pi^2 IKT}{\sigma h^2}$$

$$\therefore S_{rot} = R\left[1 + \ln\frac{8\pi^2 IKT}{\sigma h^2}\right] \text{ ——— } (4)$$

Numerically,

For linear molecule to the rotational entropy of ideal gases are given by,

$$\therefore S^{\circ}_{rot}\,(J/K\,mole) = 877.37 + 8.3143\,[\ln I + \ln T \cancel{+} - \ln \sigma] \quad \text{——(5)}$$

$[I \text{ in } Kg.m^2]$

(2) Non-linear molecules :-

Eq^n ④ and eq^n ⑤ are applicable to all diatomic molecules and all linear molecules.

Generally shaped molecules have three ~~mot~~ rotational degree of freedom.

$$\therefore (U - U_0)_{rot.} = 3/2\,RT$$

For a generally shaped molecules rotation is described in terms of components rotation about 3 perpendicular axes. The moment of inertia about these three axes are known as the principal moment of inertia and are represented by IA, IB and IC.

The rotational partition function for generally shaped molecule is,

$$\therefore q_{rot.} = \left(\frac{8\pi^2 KT}{h^2}\right)^{3/2} \cdot \left(\frac{\pi I_A I_B I_C}{\sigma}\right)^{1/2}$$

The rotational entropy for non-linear molecule is given by,

$$\therefore S_{rot} = R\left[3/2 + \ln\left(\frac{8\pi KT}{h^2}\right)^{3/2}\left(\frac{\pi I_A I_B I_C}{\sigma}\right)^{1/2}\right]$$

Numerically,

$$\therefore S^{\circ}_{rot} = (J/K\ mole) = 1320.83 + 4.153 \ln I_A I_B I_C + 12.47 \ln T - 8.3143 \ln \sigma$$

$[I_A, I_B, I_C$ in $Kg.m^2]$

⇒ Limitations :-

The equation can not be applied to molecules with very low moments of inertia (or) at very low temperatures.

* Vibrational Entropy :-

The entropy due to the vibrations of molecules can be calculated.

The vibrational thermal energy is given by,

$$\therefore (U-U_0)_{vib.} = RT \frac{x}{e^{x}-1} \text{ ——— } (1).$$

$$\text{where } x = \frac{h\nu_{vib}}{KT} \text{ ——— } (2).$$

The vibrational partition function for each vibrational degree of freedom was given by,

$$\therefore q_{vib.} = \frac{1}{1-e^{-x}} \text{ ——— } (3).$$

Thus, for each vibrational degree of freedom of the molecules of 1 mole of gas, the entropy for vibrational motion is,

$$\therefore S_{vib.} = \frac{(U-U_0)_{vib}}{T} + R \ln q_{vib} \text{ ——— } (4).$$

Substitute the value of eq^n (1) and eq^n (3) in eq^n (4), we get,

$$\therefore S_{vib} = \frac{RT}{T} \cdot \frac{x}{(e^{x}-1)} + R \ln \frac{1}{1-e^{-x}}$$

$$\therefore S_{vib.} = R \cdot \frac{x}{(e^{x}-1)} + R \ln \frac{1}{1-e^{-x}}$$

$$\therefore S_{vib} = R \left[\frac{x}{(e^{x}-1)} + \ln \frac{1}{1-e^{-x}} \right]$$

$$\therefore S_{vib} = R \left[\frac{x}{e^{x}-1} + \ln (1-e^{-x})^{-1} \right] \text{——— (5)}$$

Numerically,

$$\therefore S^{\circ}_{vib} = 8.3143 \left[\frac{x}{e^{x}-1} - \ln (1-e^{-x}) \right]$$

Ex.:- Calculate the translational entropy at 1 mole of Argon (Ar) gas at a pressure of 1 bar and a temperature of 87.3°K.

Given :-

Atomic weight of Ar = 39.95 gm/mole.

<u>Ans</u>

$$S^{\circ}_{trans} = 76.57 + 12.47 \ln M + 20.79 \ln T$$

where,

$M = 39.95 \text{ gm/mole} = 39.95 \times 10^{-3} \text{ Kg/mole}$

$T = 87.3°K$, $n = 1$, $p = 1 \text{ bar}$.

$$\therefore S^{\circ}_{trans} = 76.57 + 12.47 \ln (39.95 \times 10^{-3}) + 20.79 \ln (87.3)$$

$$\therefore S^{\circ}_{trans} = 76.57 + 12.47 (-3.2314) + 20.79 (4.4693).$$

$$\therefore S^{\circ}_{trans} = 76.57 + (-40.29) + 92.91$$

$$\boxed{\therefore S^{\circ}_{trans} = 129.19 \text{ J/K mole}}$$

Ex.:- Calculate the translational entropy of mercury vapour at 25°c.

Atomic weight of Hg = 200.61 gm/mole

Ans: $S^{\circ}_{trans} = 195.00 + 12.47 \ln M$

where

$M = 200.61$ gm/mole $= 200.61 \times 10^{-3}$ Kg/mole.

$\therefore S^{\circ}_{trans} = 195.00 + 12.47 \ln (200.61 \times 10^{-3})$.

$\therefore S^{\circ}_{trans} = 195.00 + 12.47 (-1.6063)$

$$\boxed{\therefore S^{\circ}_{trans} = 174.97 \text{ J/K.mole}}$$

Ex.:- Calculate the 25°c rotational entropy of 1 mole of CO molecules. The moment of inertia of a CO molecule is 14.50×10^{-47} Kg.m².

Ans: $S^{\circ}_{rot} = 877.37 + 8.314 [\ln I + \ln T - \ln \sigma]$

Given: $T = 25°c = 25° + 273° = 298°K$

$\sigma = 1$ mole

$I = 14.50 \times 10^{-47}$ Kg.m²

$\therefore S^{\circ}_{rot} = 877.37 + 8.3143 [\ln (14.50 \times 10^{-47}) + \ln (298) - \ln (1)]$

$\therefore S^{\circ}_{rot} = 877.37 + 8.3143 [(-105.54) + 5.6970]$

$\therefore S^{\circ}_{rot} = 877.37 + 8.3143 [-99.843]$

$\therefore S^{\circ}_{rot.} = 877.37 + (-830.12)$

$$\boxed{\therefore S^{\circ}_{rot} = 47.25 \text{ J/K.mole}}$$

Ex.:- Calculate the rotational entropy of 1 mole of CS_2 gas in its standard state. The molecule is linear and has a moment of inertia of 256×10^{-47} Kg.m².

Ans $S^{\circ}_{rot} = 877.37 + 8.3143 \left[\ln I + \ln T - \ln \sigma \right]$

Given: $I = 256 \times 10^{-47}$ Kg. m^2

$T = 298^{\circ}K$

$\sigma = 2$

$\therefore S^{\circ}_{rot} = 877.37 + 8.3143 \left[\ln (256 \times 10^{-47}) + \ln (298) - \ln (2) \right]$

$\therefore S^{\circ}_{rot} = 877.37 + 8.3143 \left[\right.$ [illegible] $(-102.676) + (5.697) - 0.6931 \left. \right]$

$\therefore S^{\circ}_{rot} = 877.37 + 8.3143 \left[-97.6721 \right]$

$\therefore S^{\circ}_{rot} = 877.37 + \left[-812.084 \right]$

$$\boxed{\therefore S^{\circ}_{rot} = 65.286 \text{ J/K.mole}}$$

Ex.:- Calculate the vibrational contribution to the entropy of 1 mole of CO at (a) 25°c and (b) 1000°c. The vibrational energy spacing factor $h\nu_{vib}$ is 4.26×10^{-20} J.

Ans: [a] At 25°c :-

$$S_{vib} = 8.3143 \left[\frac{x}{e^{x} - 1} - \ln (1 - e^{-x}) \right]$$

Given: $h\nu_{vib.} = 4.26 \times 10^{-20}$ J

$K = 1.38 \times 10^{-23}$ J/K

$T = 25^{\circ}C = 25^{\circ} + 273^{\circ} = 298^{\circ}K$

$$\therefore x = \frac{h\nu_{vib}}{KT} = \frac{4.26 \times 10^{-20}}{1.38 \times 10^{-23} \times 298} = 10.35$$

$$\therefore S^{\circ}_{vib} = 8.3143 \left[\frac{10.35}{e^{10.35} - 1} - \ln (1 - e^{-10.35}) \right]$$

$$\therefore S^{\circ}_{vib} = 8.3143 \left[\frac{10.35}{31257. - 1} - \ln (1 - 3.1992 \times 10^{-5}) \right]$$

$$\therefore S^{\circ}_{vib} = 8.3143 \left[\frac{10.35}{31256} - \ln (0.99996) \right]$$

$\therefore S^{\circ}_{vib} = 8.3143 \left[3.31136 \times 10^{-4} - (-4.0000 \times 10^{-5})\right]$

$\therefore S^{\circ}_{vib} = 8.3143 \left[3.71136 \times 10^{-4}\right]$

$\therefore S^{\circ}_{vib} = 3.0857 \times 10^{-3}$ J/K.mole

$\boxed{\therefore S^{\circ}_{vib} = 0.0030857 \text{ J/K.mole}}$

[b] At 1000°c :-

Given : $h\nu_{vib} = 4.26 \times 10^{-20}$ J

$K = 1.38 \times 10^{-23}$ J/K

$T = 1000^{\circ}c = 1000^{\circ} + 273^{\circ} = 1273^{\circ}K$

$\therefore x = \dfrac{h\nu_{vib}}{KT} = \dfrac{4.26 \times 10^{-20}}{1.38 \times 10^{-23} \times 1273} = 2.42$

$\therefore S^{\circ}_{vib} = 8.3143 \left[\dfrac{x}{e^{x}-1} - \ln(1-e^{-x})\right]$

$\therefore S^{\circ}_{vib} = 8.3143 \left[\dfrac{2.42}{e^{2.42}-1} - \ln(1-e^{-2.42})\right]$

$\therefore S^{\circ}_{vib} = 8.3143 \left[\dfrac{2.42}{11.24-1} - \ln(1-0.0889)\right]$

$\therefore S^{\circ}_{vib} = 8.3143 \left[\dfrac{2.42}{10.24} - \ln(0.9111)\right]$

$\therefore S^{\circ}_{vib} = 8.3143 \left[0.2363 - (-0.0931)\right]$

$\therefore S^{\circ}_{vib} = \cancel{813}\ 8.3143 \left[0.2363 + 0.0931\right]$

$\therefore S^{\circ}_{vib} = 8.3143 \left[0.3294\right]$

$\therefore S^{\circ}_{vib} = 2.738$ J/K.mole

$\boxed{\therefore S^{\circ}_{vib} \cong 2.74 \text{ J/K mole}}$

Ex.:- Calculate the total entropy of 1 mole of Cl_2 gas at 1 bar pressure and 25°C. The moment of inertia of Cl-molecule is 1.15×10^{-45} Kg.m² and vibrational energy level spacing is 565 cm⁻¹. Atomic weight of Cl is 35.45 gm/mole ($\because \sigma = 2$)

Ans:- $S^{\circ}_{total} = S^{\circ}_{trans.} + S^{\circ}_{rot.} + S^{\circ}_{vib.}$

(a) $S^{\circ}_{trans} = 195.00 + 12.47 \ln M$

Given: $M = 35.45$ gm/mole $= 35.45 \times 10^{-3}$ Kg/mole

$\therefore S^{\circ}_{trans} = 195.00 + 12.47 \ln[35.45 \times 10^{-3} \times 2]$

$\therefore S^{\circ}_{trans} = 195.00 + 12.47 \ln[0.0709]$

$\therefore S^{\circ}_{trans} = 195.00 + 12.47(-2.6464)$

$\therefore S^{\circ}_{trans} = 195.00 + (-33.0006)$

$\boxed{\therefore S^{\circ}_{trans} = 161.99 \text{ J/K mole}}$

(b) $S^{\circ}_{rot} = 877.37 + 8.3143 [\ln I + \ln T - \ln \sigma]$

Given: $I = 1.15 \times 10^{-45}$ Kg.m²

$T = 298°K$

$\sigma = 2$

$\therefore S^{\circ}_{rot.} = 877.37 + 8.3143[\ln(1.15 \times 10^{-45}) + \ln(298) - \ln(2)]$

$\therefore S^{\circ}_{rot.} = 877.37 + 8.3143 [(-103.47) + 5.697 - 0.6931]$

$\therefore S^{\circ}_{rot} = 877.37 + 8.3143 [-98.4661]$

$\therefore S^{\circ}_{rot.} = 877.37 + [-818.68]$

$\boxed{\therefore S^{\circ}_{rot.} = 58.69 \text{ J/K mole}}$

(c) $S^{\circ}_{vib} = 8.3143 \left[\frac{x}{e^{x}-1} - \ln(1-e^{-x})\right]$

& where

$$x = \frac{hc\bar{\nu}}{KT} = \frac{6.626 \times 10^{-34} \times 3 \times 10^{10} \times 565}{1.38 \times 10^{-23} \times 298} = 2.72$$

$$\therefore S^\circ_{vib} = 8.3143 \left[\frac{2.72}{e^{2.72} - 1} - \ln(1 - e^{-2.72}) \right]$$

$$\therefore S^\circ_{vib} = 8.3143 \left[\frac{2.72}{15.18 - 1} - \ln(1 - 0.0658) \right]$$

$$\therefore S^\circ_{vib} = 8.3143 \left[\frac{2.72}{14.18} - \ln(-0.9342) \right]$$

$$\therefore S^\circ_{vib} = 8.3143 \left[0.1918 - (-0.06806) \right]$$

$$\therefore S^\circ_{vib} = 8.3143 \left[0.25986 \right]$$

$$\boxed{\therefore S^\circ_{vib} = 2.1605 \text{ J/K mole}}$$

The total entropy is,

$$\therefore S^\circ_{total} = S^\circ_{rot.} + S^\circ_{trans.} + S^\circ_{vib.}$$

$$\therefore S^\circ_{total} = 58.69 + 161.99 + 2.1605$$

$$\boxed{\therefore S^\circ_{total} = 222.84 \text{ J/K mole}}$$

Ex. Calculate the total entropy of HCl at 25°c. The moment of inertia of HCl is 2.679×10^{-47} Kg.m^2. The vibrational energy level spacing is 2885 cm^{-1}. Atomic weight of HCl = 36.5 gm/mole.

Ans:- [a]

$$\therefore S^\circ_{trans} = 195.00 + 12.47 \ln M$$

$$\therefore S^\circ_{trans} = 195.00 + 12.47 \ln [36.5 \times 10^{-3}]$$

$$\therefore S^\circ_{trans} = 195.00 + 12.47 [-3.3104]$$

$$\therefore S^\circ_{trans.} = 195.00 + [-41.28]$$

$$\boxed{\therefore S^\circ_{trans} = 153.72 \text{ J/K mole}}$$

[b]. $S^\circ_{rot.} = 877.37 + 8.3143 [\ln I + \ln T \cancel{+} - \ln \sigma]$

where, $I = 2.679 \times 10^{-47}$ Kg.m^2

$T = 25°c = 25° + 273° = 298°K$

$\sigma = 1.$

$\therefore S^\circ_{rot} = 877.37 + 8.3143\left[\ln(2.679 \times 10^{-47}) + \ln(298)\right]$

$\therefore S^\circ_{rot.} = 877.37 + 8.3143\left[(-107.23) + 5.697\right]$

$\therefore S^\circ_{rot} = 877.37 + 8.3143\left[-101.533\right]$

$\therefore S^\circ_{rot} = 877.37 + \left[-844.175\right]$

$\boxed{\therefore S^\circ_{rot} = 33.195\ J/K\ mole}$

[c] $S^\circ_{vib} = 8.3143\left[\dfrac{x}{e^{x}-1} - (1 - e^{-x})\right]$

where,

$x = \dfrac{hc\bar{\nu}}{KT} = \dfrac{6.626 \times 10^{-34} \times 3 \times 10^{10} \times 2885}{1.38 \times 10^{-23} \times 298} = 13.94.$

$\therefore S^\circ_{vib.} = 8.3143\left[\dfrac{13.94}{e^{13.94}-1} - (1 - e^{(-13.94)})\right]$

$\therefore S^\circ_{vib} = 8.3143\left[\dfrac{13.94}{1.1325 \times 10^{6} - 1} - \ln(1 - 8.8294 \times 10^{-7})\right]$

$\therefore S^\circ_{vib} = 8.3143\left[1.2309 \times 10^{-5} - (-1.0000 \times 10^{-4})\right]$

$\therefore S^\circ_{vib} = 8.3143\left[1.12309 \times 10^{-4}\right]$

$\therefore S^\circ_{vib} = \cancel{8.3143}\ 9.3377 \times 10^{-4}$

$\boxed{\therefore S^\circ_{vib} = 0.000933\ J/K\ mole}$

$\therefore S^\circ_{total} = S^\circ_{trans.} + S^\circ_{rot.} + S^\circ_{vib.}$

$\therefore S^\circ_{total} = 153.72 + 33.195 + 0.00093377$

$\boxed{\therefore S^\circ_{total} = 186.91\ J/K.mole}$

* Trouton's Rule :- The entropies of vaporization of liquids.

An empirical generalisation about the entropy of vapourization of a liquid is known as Trouton's Rule.

Trouton's rule stated that, "the enthalpy of vapourization of a liquid (ΔH_{vap}) divided by normal boiling point (T_b) is approximately the same for all liquids."

i.e. $$\frac{\Delta H_{vap}}{T_b} \cong 88.0 \text{ J/K.mole (constant)}$$

The ratio of enthalpy of vapourization to temperature measuring the entropy of vapourization,

$$\therefore \Delta S_{vap} = \frac{d\,q_{rev}}{T} = \frac{\Delta H_{vap}}{T} = \text{constant}$$

In other words, Trouton's rule stated that, "the entropy increases by the same amount when one mole of any liquids is changed to vapour at its normal boiling point."

This rule is remarkable for simple and complex inorganic compounds, organic compounds, an ionic substances and several metals.

For ΔS_{vap} the entropy of one mole of (substance) molecules in vapour must be compared with the entropy of one mole of liquid molecules at equilibrium. The entropies are described in terms of translational, rotational and vibrational contribution.

For most of the molecules, the vibrational and rotational contributions to the entropy are same for liquid phase and gas phase molecules in equilibrium. However, the translational entropies of liquid and vapour in equilibrium are not the same and hence play an important role.

The translational entropy of vapour phase includes the term $R \ln V$. The translational entropy of molecules of liquid phase can be treated in terms of volume of liquid in which molecules are free to move. This volume is called Free - volume and is represented as V_f.

Entropy of transformation from liquid to vapour state is given by,

$$\therefore \Delta S_{vap} = S_v - S_l = R \ln \frac{V_v}{V_f}$$

where,

V_v = The volume of one mole of vapour at equilibrium

V_f = The free-volume of a liquid at equilibrium

The value of ΔS_{vap} is insensitive to value of V_v/V_f.

*** Limitations :-**

(1) Trouton's rule is not applicable to substance having very low boiling point. The ΔS_{vap} values are less than the average expected values for H_2 and He.

For H_2, $\Delta S_{vap} = 44.3$

For He, $\Delta S_{vap} = 20.0$

(2) Trouton's rule is not valid for all liquids which have tendency to undergo association (or) dissociation.

(3) The substance forming dimers like acetic acid and formic acid show ΔS_{vap} less than expected, due to their tendency to form hydrogen bonding even in gas phase.

(4) The substance like water, alcohol shows ΔS_{vap} higher than the ~~averg~~ average value, due to molecular association in liquid phase due to H-bondings.

~~* Free - Bondi~~

☆ Free - Energy:

Free-energy is a property that provides a convenient measure of the driving force of a reaction.

Consider a chemical system in which a reaction occurs at constant temperature and constant pressure.

The entropy change of the thermal surroundings, $\frac{\Delta U_{thermal}}{T}$ is $-\frac{\Delta H}{T}$

The entropy change of the universe of the reaction system is given by,

$$\therefore \Delta S_{uni.} = \Delta S + \Delta S_{thermal} \quad \text{——— (1)}$$

$$\text{but } \Delta S_{thermal} = -\frac{\Delta H}{T} \quad \text{——— (2)}$$

substitute the value of $\Delta S_{thermal}$ in eq^n (1), we get,

$$\therefore \Delta S_{uni.} = \Delta S - \frac{\Delta H}{T} \quad \text{——— (3)}$$

Eq^n ③ can be calculated from changes in the properties of the system.

Eq^n ③ multiply by T, we get,

$$\Delta S_{uni.} T = \Delta S \cdot T - \frac{\Delta H}{\cancel{T}} \cdot \cancel{T} \quad \text{———— (4)}$$

but $T \cdot \Delta S_{uni.} = -\Delta G$ ———— (5).

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

(or)

$\therefore \Delta G = \Delta H - T \cdot \Delta S$ ———— (6).

Thus, the change in the free-energy of a system, for any constant temperature process is equal to the change in the enthalpy minius the product of the absolute temperature and the change in the entropy.

Conclusions:

(1) If ΔG is negative, the reaction is spontaneously.

(2) If ΔG is positive, the reverse reaction can proceed spontaneously.

(3) If ΔG is zero, the reaction would proceed reversibly (or) at a state of balance.

* Free-Energy and Pressure :-

Free-energy of a gas depends on the pressure that confines the gas.

From the free-energy defination equations,

$\therefore G = H - T \cdot S$ ———— (I)

Differentiate eq^n (I), we get,

$\therefore dG = dH - d(T \cdot S)$

$\therefore dG = dH - T \cdot dS - S \cdot dT$ ———— (2).

but

$H = U + PV$ ———— (3)

differentiate the eq^n (3), we get,

$\therefore dH = dU + d(P.V)$

$\therefore dH = dU + PdV + V.dP$ ——— (4)

Substitute the value of dH in eq^n (2), we get,

$\therefore dG = dU + P.dV + V.dP - T.dS - S.dT$ ——— (5)

In an "ordinary process" in which no mechanical energy other than P.dV energy is involved. In this case,

$\therefore PdV = dU_{mech}$ ——— (6)

Imagine that the states of the system that we are considering can be connected by a reversible process. For such a process,

$\therefore T.ds = -dU_{thermal}$ ——— (7)

Substitute the value of eq^n (6) and eq^n (7) in eq^n (5), we get,

$\therefore dG = dU + dU_{mech.} + V.dP + dU_{thermal} - S.dT$ ——— (8)

According to 1st law of thermodynamics, energy of universe is constant.

$\therefore$ All U terms tends to zero [$\because dU, dU_{mech.} \& dU_{thermal} = 0$]

Eq^n (8) becomes,

$\therefore dG = V.dP - S.dT$ ——— (9)

This expression for changes in the free-energy in terms of changes in just two state-determing variables.

The free-energy G as a property of the system and therefore, dependent on the state of the system.

If this state is specified by the temperature and the pressure, we can write the general total differential,

$$\therefore dG = \left(\frac{dG}{dP}\right)_T . dP + \left(\frac{dG}{dT}\right)_P . dT \quad \text{———} (10)$$

Compared the eq^n (10) with eq^n (9), let us make the identification,

$$\therefore \left(\frac{dG}{dP}\right)_T = V \text{ and } \left(\frac{dG}{dT}\right)_P = -S .$$

This equation shows the change in the free-energy property with respect to change in temperature and pressure.

This dependence of free-energy on temperature, the expression obtained for the pressure dependence.

Liquids and solids have small molar volumes compared with gases. For many purpose the pressure dependence of the free-energy of liquids and solids can be neglected.

Eq^n (9) becomes,

$$\therefore dG = V.dp - SdT$$

At constant temperature,

$$\therefore dT = 0 , \quad S.dT = 0$$

$$\therefore dG = V.dP \quad \text{———} (11)$$

For gases the dependence of free-energy on pressure is appreciable and important. For an ideal gas, P and V are related by the ideal gas law and the integrating eq^n (11),

$$\therefore \int dG = \int V . dp$$

The free-energy change when the pressure is changed from P_1 to P_2.

Thus,

$$\therefore \int_1^2 dG = \int_{P_1}^{P_2} V . dP$$

$$\therefore G_2 - G_1 = \int_{P_1}^{P_2} V . dP \quad \text{——— (12)}$$

For ideal gas,

$$PV = nRT$$

$$\therefore V = \frac{nRT}{P} \quad \text{——— (13)}$$

Substitute the value of V in eq^n (12), we get

$$\therefore G_2 - G_1 = \int_{P_1}^{P_2} \frac{nRT}{P} . dp$$

$$\therefore G_2 - G_1 = nRT \int_{P_1}^{P_2} dP/p$$

$$\therefore G_2 - G_1 = nRT \ln P_2/P_1 \quad \text{——— (14)}$$

The free-energy changes from standard state value, when the pressure changes from 1 bar and ideal gas are 1 mole.

when, $P_1 = 1$ bar and $G_1 = G^\circ$

$P_2 = P$ bar and $G_2 = G$

$$\therefore G_2 - G_1 = nRT \ln P_2/P_1$$

$$\therefore G - G^\circ = RT \ln P/1$$

$$\therefore G - G^\circ = RT \ln P \quad \text{——— (15)}$$

[Temperature constant, P in 1 bar and 1 mole of ideal gas]

This equation is strictly applicable for ideal gases.

* Free-Energy and the equilibrium constant :-

The equilibrium constant is related to the standard-free energy change by the relation,

$$\Delta G^\circ = -RT\ln K \quad \text{———} \quad (1)$$

Consider a reaction involving four gases A, B, C and D in a reaction system at a temperature T and a total pressure P.

Assume these gases can enter into a reaction,

$$\therefore aA + bB \longrightarrow cC + dD$$

where, a, b, c and d are the numbers of moles of each reagent involved.

The free-energies of a mole of A at a pressure P_A, b mole of B at a pressure P_B and so on, can be written as,

Free-energy of a mole A $= aG_A = aG^\circ_A + aRT\ln P_A$.

Free-energy of b mole B $= bG_B = bG^\circ_B + bRT\ln P_B$.

Free-energy of c mole C $= cG_C = cG^\circ_C + cRT\ln P_C$

Free-energy of d mole D $= dG_D = dG^\circ_D + dRT\ln P_D$.

The free-energy change for the reaction, when the pressures of the four spaces are P_A, P_B, P_C and P_D respectively, can be calculated as,

$$\therefore \Delta G = G_{product} - G_{Reactant}.$$

$$\therefore \Delta G = [cG_C + dG_D] - [aG_A + bG_B]$$

$\therefore \Delta G = [cG^\circ_C +$ ~~$dG_D] = [$~~ $RT\ln(P_C)^c + dG^\circ_D + RT\ln(P_D)^d]$

$- [aG^\circ_A + RT\ln(P_A)^a + bG^\circ_B + RT\ln(P_B)^b]$

$$\therefore \Delta G = cG^\circ_C + dG^\circ_D - aG^\circ_A - bG^\circ_B + RT\ln\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \quad \text{———} (2)$$

but,

$$\Delta G^\circ = G^\circ_{product} - G^\circ_{reactant}$$

$$\therefore \Delta G^\circ = [cG^\circ_C + dG^\circ_D] - [aG^\circ_A + bG^\circ_B] \quad \text{———} (3).$$

Eq^n ② becomes,

$$\therefore \Delta G = \Delta G^\circ + RT\ln\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \quad \text{———} (4).$$

Equation (4) relates the free-energy change of the reaction for the reagents at pressures P_A, P_B, P_C, P_D to a term involving the free-energies of all reagents at 1-bar pressure and a term for all the free-energy pressure dependence.

If ~~all~~ the reaction system is allowed to proceed to a state of equilibrium with respect to this reaction. It will reach a position for which no further driving force is operative.

The free-energy will be a minimum and any small change in the state of the system must be accompanied by a zero free-energy.

At equilibrium, $\Delta G = 0$

Eq^n (4) becomes,

$$\therefore \Delta G^\circ = -RT\ln\left[\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}\right]_{equi.} \quad \text{———} (5).$$

where the subscript equilibrium is added, when the pressures are those of the system at equilibrium.

$$\text{but}\quad \left[\frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}\right]_{equi.} = K_p \quad \text{———} (6).$$

∴ Equation (5) becomes,

$$\therefore \Delta G^{\circ} = -RT \ln K_p \quad \text{———} (7)$$

Eq^n (7) shows relation between free-energy and equilibrium constant.

* Free-Energy and Temperature :-

The way in which free-energy depends on temperature shows the way in which the equilibrium constant depends on temperature.

The free-energy of each substance involved in a reaction depends on the temperature as,

$$\therefore \left(\frac{dG}{dT}\right)_P = -S \quad \text{———} (1)$$

Eq^n (1) is applied to each of the reagents, the relation is,

$$\therefore \left[\frac{d(\Delta G)}{dT}\right]_P = -\Delta S \quad \text{———} (2)$$

At any constant temperature, the changes of free-energy, enthalpy and entropy for any reaction are related by,

$$\therefore \Delta G = \Delta H - T.\Delta S \quad \text{———} (3)$$

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

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

Substitute the value of ΔS in eq^n (2), we get,

$$\therefore \left[\frac{d(\Delta G)}{dT}\right]_P = -\frac{\Delta H - \Delta G}{T}$$

$$\therefore \left[\frac{d(\Delta G)}{dT}\right]_P = -\frac{\Delta H}{T} + \frac{\Delta G}{T} \quad \text{or} \quad \therefore \left[\frac{d(\Delta G)}{dT}\right]_P - \frac{\Delta G}{T} = \frac{-\Delta H}{T}$$

$$\text{———} (5)$$

The two term on the left side of eq^n (5) can be shown to be equivalent to,

$$T\left[\frac{d(\Delta G/T)}{dT}\right]_p = T \;\; \frac{T\left[d(\Delta G/dT)\right]_p - \Delta G}{T^2}$$

$$\therefore T\left[\frac{d(\Delta G/T)}{dT}\right]_p = \left[\frac{d(\Delta G)}{dT}\right]_p - \frac{\Delta G}{T} \quad \text{——— (6)}$$

Left side of eq^n (6) can be inserted in place of the left side eq^n (5) to give,

$$\therefore T\left[\frac{d(\Delta G/T)}{dT}\right]_p = -\frac{\Delta H}{T} \quad \text{——— (7)}$$

Standard states are indicated and the relation $\Delta G^\circ = -RT\ln K$ is inserted to give, on rearrangement,

$$\therefore \frac{d(\ln K)}{dT} = \frac{\Delta H^\circ}{RT^2}$$

This important formula is the goal of the derivation. The rate change of the equilibrium constant with temperature is seen to depend on the standard enthalpy change.

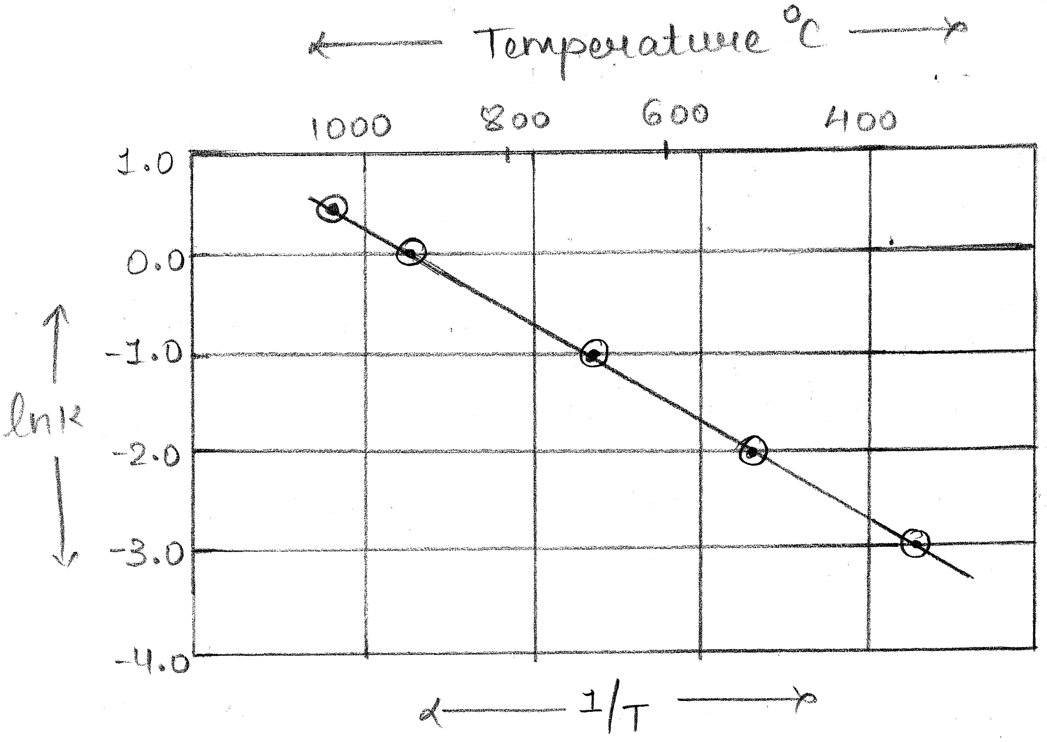
Rearranging eq^n (8), we get,

$$\therefore \frac{d(\ln K)}{d(1/T)} = \frac{\Delta H^\circ}{R} \quad \text{——— (9)}$$

On integrating eq^n (9), on the assumption that ΔH° is independent temperature is,

$$\therefore \ln K = -\frac{\Delta H^\circ}{RT} + \text{constant} \quad \text{——— (10)}$$

Plot the graph lnK against $1/T$. The graph is straight line and slope is equal to $-\frac{\Delta H^\circ}{R}$



* Free - Energy Function :-

Free - energy is the property that connects thermodynamic equilibrium to chemical equilibrium at any temperature. The value of free - energy function can be developed from calorimetric data (or) from the properties of molecules of the substance.

* Free - Energy from calometric Data :-

If heat capacity data and the enthalpy values are available at 25°c then the free-energy values at various temperature can be determined.

we know that, free - energy of substance at any temperature is given by,

$$\therefore G = H^\circ - T.S^\circ \quad \text{———} (1)$$

The free-energy of any substance at some temperature can be developed by substracting the enthalpy of the substance at the ~~substance~~ reference temperature 298°K

$$\therefore G^{\circ} - H^{\circ}_{298} = H^{\circ} - H^{\circ}_{298} - T.S^{\circ} \quad \text{———} (2)$$

Dividing by T leads to less temperature-dependent quantities,

$$\therefore \frac{G^{\circ} - H^{\circ}_{298}}{T} = \frac{H^{\circ} - H^{\circ}_{298}}{T} - \frac{T.S^{\circ}}{T}$$

$$\therefore \frac{G^{\circ} - H^{\circ}_{298}}{T} = \frac{H^{\circ} - H^{\circ}_{298}}{T} - S^{\circ} \quad \text{———} (3)$$

The value of the R.H.S can be evaluated from calorimetric data and the quantity $\left(\frac{G^{\circ} - H^{\circ}_{298}}{T}\right)$ is known as the free-energy function.

This free-energy function has negative values at all temperatures above 298°K, it is represented as $-\left(\frac{G^{\circ} - H^{\circ}_{298}}{T}\right)$ and the unit is joule (or) Kilojoules.

* Free-Energy and molecular properties :-

The standard free-energy is given by the defining equation,

$$\therefore G^{\circ} = H^{\circ} - T.S^{\circ} \quad \text{———} (1)$$

on subtracting the thermal energy at °K

$$\therefore G^{\circ} - U^{\circ}_{0} = H - U^{\circ}_{0} - T.S^{\circ} \quad \text{———} (2)$$

But for ideal gas,

$$\therefore H^{\circ} - U^{\circ}_{0} = U^{\circ} - U^{\circ}_{0} + RT \quad \text{———} (3)$$

and

$$S^\circ = \frac{U^\circ - U_0^\circ}{T} + R \ln \frac{q^\circ}{N} + R \text{ ——— } (4).$$

Substitute the value of eq^n (3) & eq^n (4) in eq^n (2), we get,

$$\therefore G^\circ - U_0^\circ = (U^\circ - U_0^\circ) + RT - T\left[\frac{U^\circ - U_0^\circ}{T} + R \ln \frac{q^\circ}{N} + R\right]$$

$$\therefore G^\circ - U_0^\circ = U^\circ - U_0^\circ + RT - \frac{\cancel{T}(U^\circ - U_0^\circ)}{\cancel{T}} - RT \ln \frac{q^\circ}{N} - RT$$

$$\therefore G^\circ - U_0^\circ = \cancel{U^\circ} - \cancel{U_0^\circ} + \cancel{RT} - \cancel{U^\circ} + \cancel{U_0^\circ} - RT \ln \frac{q^\circ}{N} - \cancel{RT}$$

$$\boxed{\begin{gathered} \therefore G^\circ - U_0^\circ = -RT \ln \frac{q^\circ}{N} \\ \text{(or)} \\ \therefore \frac{G^\circ - U_0^\circ}{T} = -R \ln \frac{q^\circ}{N} \\ \text{(or)} \\ \therefore G^\circ = U_0^\circ - RT \ln \frac{q^\circ}{N} \end{gathered}}$$

(ideal gas).

This is the molecular basis of the free-energy property. The standard free-energy G° is equal to the energy U_0° that the system would have if all the molecules were in their lowest-energy state modified by a term $RT \ln q^\circ/N$ which involves the ~~position~~ partition function.

* Free - Energy function from molecular properties :-

The thermal contribution to the standard state free-energy of an ideal gas is,

$\therefore G^\circ - U_0^\circ = -RT \ln \frac{q^\circ}{N}$

The free-energy quantity $G^\circ - U_0^\circ$ like $G^\circ - H_{298}^\circ$, increases sharply with temperature. and its value is negative at all temperature.

Again, dividing by T and introduced by -ve sign : we get another free-energy function based on °K rather than 298K.

$\therefore -\frac{G^\circ - U_0^\circ}{T} = R \ln \frac{q^\circ}{N}$

This free-energy function completes the list of the thermodynamic properties that are calculated for ideal gases.

Summary of expressions used for calculation of thermodynamic functions from properties of molecules of an ideal gas.

	Translational	Linear	Rotational Non-linear	Vibrational.
$q = q_1 + q_2 + q_3$	$q_t = \left(\frac{2\pi mKT}{h^2}\right)^{3/2}$	$q_t = \left(\frac{2IKT}{\sigma h^2}\right)$	$q_t = \left(\frac{2IKT}{h^2}\right)^{3/2}\left(\frac{\pi I_A I_B I_C}{\sigma}\right)^{1/2}$	$q_t = \frac{1}{1-e^{-x}}$.
$U - U_0^\circ = \frac{RT^2}{q} \cdot \frac{dq}{dT}$	$3/2\ RT$	RT	$3/2\ RT$	$RT \cdot \frac{x}{e^x - 1}$.
$H - U_0 = U - U_0 + RT$	$5/2\ RT$	RT	$3/2\ RT$	$RT \cdot \frac{x}{e^x - 1}$.
$C_v = \frac{d}{dT}(U - U_0)$.	$3/2\ RT$	R	$3/2\ R$	$Rx^2 \cdot \frac{ex}{(e^x - 1)^2}$
$S = \frac{U - U_0}{T} + R\ln\frac{q}{N} + R$	$5/2\ R + R\ln\frac{q_t}{N}$	$R + R\ln q_r$	$3/2\ R + R\ln q_r$.	$\frac{Rx}{(e^x - 1)} + R\ln q_r$
$-\frac{G - U_0}{T} + R\ln\frac{q}{N}$	$R\ln\frac{q_t}{N}$	$R\ln q_r$	$R\ln q_r$	$R\ln q_r$.

* Equilibrium constant from Free-Energy Function :-

The change in the free-energy that accompanies a chemical reaction can be calculated from the free-energy function values.

The basic relations that can be applied at any temperature are,

$$\therefore \frac{\Delta G^\circ}{T} = \frac{\Delta[G^\circ - H^\circ_{298}]}{T} + \frac{\Delta H^\circ_{298}}{T}$$

but $\Delta H^\circ_{298} = U^\circ_0$

$$\therefore \frac{\Delta G^\circ}{T} = \frac{\Delta[G^\circ - U^\circ_0]}{T} + \frac{U^\circ_0}{T}$$

The H°_{298} values can be calculated from values of standard enthalpies of formation at 298°K and U°_0 values from standard enthalpies (or) energies of formation at °K.

Conversion of free-energy functions can be made using the equation.

$$\therefore G^\circ - H^\circ_{298} = G^\circ - U^\circ_0 - [H^\circ_{298} - U^\circ_0]$$

$$\therefore G^\circ - U^\circ_0 = (G^\circ - H^\circ_{298}) + [H^\circ_{298} - U^\circ_0]$$

Ex.: Calculate the free-energy function based on 298°K for $NaCl_{(c)}$ at 1000°K. If $S^\circ_{298} = 72.13$ J/K mole and value of $a = 45.94$, $b = 16.32 \times 10^{-3} T$, $c = 0$

Ans: $$\frac{G^\circ - H^\circ_{298}}{T} = \frac{H^\circ - H^\circ_{298}}{T} - S^\circ$$

Now,

$$H^\circ - H^\circ_{298} = \int_{T_1}^{T_2} Cp \cdot dT$$

where, $C_p = a + bT + cT^2 + \text{-----}$

$$\therefore H^\circ - H^\circ_{298} = \int_{298}^{1000} [45.94 + (16.32 \times 10^{-3})T]\, dT$$

$$\therefore H^\circ - H^\circ_{298} = \int_{298}^{1000} 45.94\, dT + \int_{298}^{1000} 16.32 \times 10^{-3} T . dT$$

$$\therefore H^\circ - H^\circ_{298} = 45.94\,[1000 - 298] + 1/2\,(16.32 \times 10^{-3})\,[(1000)^2 - (298)^2]$$

$$\therefore H^\circ - H^\circ_{298} = 45.94[702] + [8.16 \times 10^{-3}]\,[911196]$$

$$\therefore H^\circ - H^\circ_{298} = 32249.88 + \cancel{40}\ 7435.35$$

$$\boxed{\therefore H^\circ - H^\circ_{298} = 39685.23\, J/K}$$

Dividing by T

$$\therefore \frac{H^\circ - H^\circ_{298}}{T} = \frac{39685.23}{1000} = 39.685\, J/K$$

Now,

$$S^\circ = S^\circ_{298} + S^\circ - S^\circ_{298}$$

$$\therefore S^\circ = 72.13 + \int_{298}^{1000} C_p/T \cdot dT$$

$$\therefore S^\circ = 72.13 + \int_{298}^{1000} \frac{45.94}{T} . dT + \left[\frac{16.32 \times 10^{-3} \cancel{T}}{\cancel{T}}\right] dT$$

$$\therefore S^\circ = 72.13 + \int_{298}^{1000} 45.94\, dT/T + \int_{298}^{1000} (16.32 \times 10^{-3})\, dT$$

$$\therefore S^\circ = 72.13 + 45.94 \ln \frac{T_2}{T_1} + (16.32 \times 10^{-3})(T_2 - T_1).$$

$$\therefore S^\circ = 72.13 + 45.94 \ln \frac{1000}{298} + (16.32 \times 10^{-3})(1000 - 298)$$

$$\therefore S^\circ = 72.13 + 45.94 \ln[3.3557] + (16.32 \times 10^{-3})(702)$$

$$\therefore S^\circ = 72.13 + 55.617 + 11.456$$

$$\boxed{\therefore S^\circ = 139.203\, J/K}$$

$$\text{Now, } \frac{G^\circ - H^\circ_{298}}{T} = \frac{H^\circ - H^\circ_{298}}{T} - S^\circ$$

$$\therefore \frac{G^\circ - H^\circ_{298}}{T} = 39.685 - 139.203$$

$$\boxed{\therefore \frac{G^\circ - H^\circ_{298}}{T} = -99.518 \text{ J/K}}$$

$$\boxed{\therefore \Delta(G^\circ - H^\circ_{298}) = -155.53 \text{ KJ}}$$

Now,

$$\begin{array}{llll} & CaCO_{3(c)} \longrightarrow & CaO_{(c)} + & CO_{2(g)} \\ \Delta H^\circ_{f298} & -1206.92 & -635.09 & -393.51 \text{ KJ} \end{array}$$

$$\therefore \Delta H^\circ = [-635.09 + (-393.51)] - [-1206.92]$$

$$\therefore \Delta H^\circ = [-1028.6] - [-1206.92]$$

$$\boxed{\therefore \Delta H^\circ = 178.32 \text{ KJ}}$$

$$\text{Then, } \Delta G^\circ = \Delta(G^\circ - H^\circ_{298}) + \Delta H^\circ_{298}$$

$$\therefore \Delta G^\circ = -155.53 + 178.32$$

$$\boxed{\therefore \Delta G^\circ = 22.79 \text{ KJ}}$$

Now, $\Delta G^\circ = -RT \ln K$ where,

$\therefore 22.79 = -8.314 \times 1000 \times \ln K \times 10^{-3}$

$\Delta G^\circ = 22.79$ KJ

$T = 1000°K$

$R = 8.314$ J

$= 8.314 \times 10^{-3}$ KJ

$$\therefore \ln K = \frac{-22.79}{8.314}$$

$$\therefore \ln K = -2.74$$

$$\therefore K = \text{Inv. } \ln[-2.74]$$

$$\boxed{\therefore K = 0.064 \text{ Bar}}$$

Now,

1 bar = 750.12 mmHg

∴ 0.064 bar = (?)

= 0.064 × 750.12

$\boxed{= 48 \text{ mmHg}}$

* Equilibria and Distributions:-

The equilibrium constant can be treated as a particular type of molecular distribution.

Consider the simple gas phase reaction, one in which molecules of A are converted to molecules of B.

$A \rightleftharpoons B$ the reaction will proceed until the state of equilibrium is reached.

At a given temperature, there will be some ratio of the number of B molecules to the number of A molecules.

Consider the generalized patterns of energies of the states of the chemical species A and B in their standard states of lowest energy is $\varepsilon_0^B - \varepsilon_0^A = \Delta\varepsilon_0$. This quantity is similar to molar quantity $U_0^B - U_0^A = \Delta U_0$, the difference in energy between 1 mole of A and 1 mole of B when all the molecules of both species are in their lowest possible energy states.

If a large number of molecules are allowed to equilibrate and distribute themselves throughout the energy level pattern then how many will occupy the A levels and how many will occupy the B levels will be calculated by Boltzman distribution.

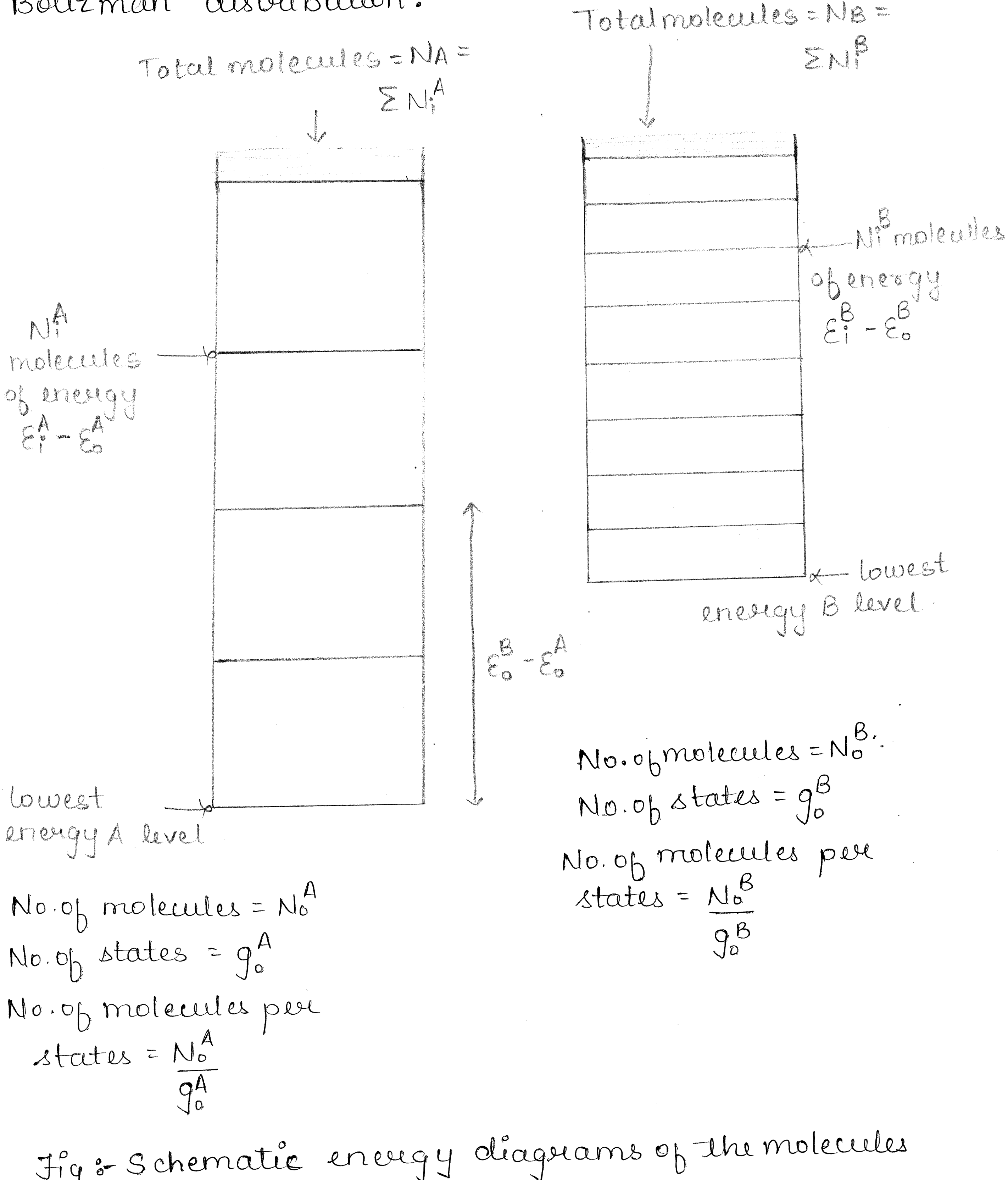


Fig :- Schematic energy diagrams of the molecules of reagents A and B connected by the equilibrium $A \rightleftharpoons B$.

The ratio of the number of A molecules occupying the lowest energy level is determined with the help of Boltzman distribution expression.

Let N_0^A be the no. of molecules occupying the lowest energy level ~~to~~ at equilibrium.

The total no. of molecules in the A levels (N_A) is given by,

$$\therefore \frac{N_A}{q_A} = \frac{N_0^A}{g_0^A}$$

$$\boxed{\therefore N_A = \left(\frac{N_0^A}{g_0^A}\right) q_A} \text{ ——— } (1).$$

Similarly, the no. of molecules N_B distributed throughout the B levels is related to that of the lowest energy B state is,

$$\boxed{\therefore N_B = \left(\frac{N_0^B}{g_0^B}\right) q_B} \text{ ——— } (2).$$

Since equilibrium is established between the distribution throughout the A and B states, the population of the lowest B state is related to the population of the lowest A state by the Boltzman expression.

$$\therefore \frac{N_0^B/g_0^B}{N_0^A/g_0^A} = e^{-\Delta E_0/KT}$$

$$\boxed{\therefore \frac{N_0^B}{g_0^B} = \left(\frac{N_0^A}{g_0^A}\right) e^{-\Delta E_0/KT}} \text{ ——— } (3).$$

Substitute the value of $\frac{N_0^B}{g_0^B}$ in eq^n(2), we get,

$$\therefore N_B = \left(\frac{N_0^A}{g_0^A}\right) e^{-\Delta\varepsilon_0/KT} \cdot q_B \text{ ——— } (4)$$

The equilibrium constant for the reaction of A and B can also be expressed as the ratio of pressure or the concentration of B to A. Both the terms are proportional to the number of moles or molecules of the two reagents.

$$\boxed{\therefore K = \frac{N_B}{N_A}} \text{ ——— } (5)$$

Substitute the value of eq^n(1) and eq^n(4) in eq^n(5), we get,

$$\therefore K = \frac{(N_0^A/g_0^A)\, e^{-\Delta\varepsilon_0/KT} \cdot q_B}{(N_0^A/g_0^A) \cdot q_A}$$

$$\boxed{\therefore K = e^{-\Delta\varepsilon_0/KT} \cdot \frac{q_B}{q_A}} \text{ ——— } (6)$$

$$\boxed{\therefore K = e^{-\Delta U_0/RT} \cdot \frac{q_B}{q_A}} \text{ ——— } (7)$$

The K depends upon values of ΔU_0 and q_B/q_A. Hence, we can say from eq^n(6) and eq^n(7) that, The formation of B is favoured by ΔU_0 values that are small or negative.

This term is temperature independent although it contains temperature dependent ~~upon~~ term $e^{-\Delta U_0/RT}$ and is not determined by the pattern of energy levels. The formation of B is also favoured by a large value of q_B relative to that of q_A.

Large partition values results when many states are available to the molecules. The formation of B will be favoured if the energies of the states of B are closely spaced and the number of states corresponding to these allowed energies is high.

The partition function can be calculated as,

$$\therefore q_A = \sum_i (g_i e^{-\Delta \varepsilon_i/KT}) = g_0^A e^{-0/KT} = (2)(1) = 2$$

$$\therefore q_B = \sum_i (g_i e^{-\Delta \varepsilon_i/KT}) = g_0^B e^{-0/KT} = (3)(1) = 3.$$

The equilibrium constant for the system can be calculated at two temperature 25°C and 1000°C.

$$\therefore K = e^{-\Delta U_0^0/RT} \cdot q_B/q_A$$

$$\therefore K_{298} = e^{-1200/8.314 \times 298} \times (3/2) = 0.92$$

$$\therefore K_{1273} = e^{-1200/8.314 \times 1273} \times (3/2) = 1.34$$

At the lower temperature, the energy term ΔU_0^0 dominates and A is favoured over B while at lower temperature B is favoured over A.

* Free-Energy and equilibrium constant :-

The standard free-energy of an ideal gas substance is related to the partition function by the relation is $G_i^0 = U_0^0 - RT \ln q^0/N$.

The standard free-energy change for a reaction is related to the equilibrium constant by $\Delta G_i^0 = -RT \ln K$

This leads to the simple reaction between the partition functions of the reagents and the equilibrium constants for the reaction.

* Consider a general reaction,

$$A \rightarrow B$$

From $G^\circ = U_0^\circ - RT \ln q^\circ/N$ for each reagents, we form,

$$\Delta G^\circ = \Delta U_0^\circ - RT \ln \frac{q_B^\circ/N}{q_A^\circ/N} \quad \text{and} \quad \Delta G^\circ = -RT \ln K$$

Compared above this two equations, we get

$$\therefore -RT \ln K = \Delta U_0^\circ - RT \ln \frac{q_B^\circ/N}{q_A^\circ/N}$$

$$\therefore \ln K = -\frac{\Delta U_0^\circ}{RT} + \frac{\cancel{R}T}{\cancel{R}T} \ln \frac{q_B^\circ/\cancel{N}}{q_A^\circ/\cancel{N}}$$

$$\therefore \ln K = -\frac{\Delta U_0^\circ}{RT} + \ln \frac{q_B^\circ}{q_A^\circ}$$

$$\therefore \ln K = \ln \frac{q_B^\circ}{q_A^\circ} - \frac{\Delta U_0^\circ}{RT}$$

$$\therefore \ln K - \ln \frac{q_B^\circ}{q_A^\circ} = -\frac{\Delta U_0^\circ}{RT}$$

$$\therefore \ln \left(K \cdot q_B^\circ/q_A^\circ\right) = -\frac{\Delta U_0^\circ}{RT}$$

$$\therefore K \cdot \frac{q_B^\circ}{q_A^\circ} = e^{-\Delta U_0^\circ/RT}$$

$$\boxed{\therefore K = e^{-\Delta U_0^\circ/RT} \cdot \frac{q_B^\circ}{q_A^\circ}}$$

* Consider a complex gas phase reaction,

$aA + bB \longrightarrow cC$

For each reagent we can use $G = U_0^\circ - RT\ln q^\circ/N$ to express can be combine to give,

$$\therefore \Delta G^\circ = \Delta U_0^\circ - RT\ln \frac{(q_C^\circ/N)^c}{(q_A^\circ/N)^a (q_B^\circ/N)^b}$$

and $\Delta G^\circ = -RT\ln K$

$$\boxed{\therefore K = \frac{(q_C^\circ/N)^c}{(q_A^\circ/N)^a (q_B^\circ/N)^b} \cdot e^{-\Delta U_0^\circ/RT}}$$

* Fugacity :- Fugacity f is a function introduced to calculate the free energy change ΔG of a non-ideal gas with pressure. It is the corrected pressure like quantity applicable to real gases. Fugacity is the term proportional to the pressure of a gas. For ideal gas its fugacity becomes equal to the pressure.

i.e.

$\lim_{P\to 0} f/P = 1$ ---- for ideal gas.

$\lim_{P\to 0} f/P \neq 1$ ---- for non-ideal gas.

If G_1 and G_2 are the molar free-energy of a gas at the pressure P_1 and P_2 and fugacity f_1 and f_2 at this pressure.

The change in free-energy

~~$\therefore G_2 =$~~ $\boxed{\therefore G_2 - G_1 = RT\ln f_2/f_1}$ ——— (1).

For ideal gas the fugacity is proportional to the pressure but non-ideal gas, the fugacity deviates from its pressure.

For one mole of gas, the change in free-energy with pressure at constant temperature given by,

$$\left(\frac{dG}{dp}\right)_T = V$$

$$\therefore G_2 - G_1 = \int_{P_1}^{P_2} V \cdot dP \quad \text{—— (2)}$$

For one mole of ideal gas

$$PV = RT$$

$$\boxed{\therefore V = \frac{RT}{P}}$$

$$\therefore G_2 - G_1 = \int_{P_1}^{P_2} RT/p \cdot dP$$

$$\therefore G_2 - G_1 = RT \int_{P_1}^{P_2} dP/p$$

$$\therefore G_2 - G_1 = RT [\ln P]_{P_1}^{P_2}$$

$$\boxed{\therefore G_2 - G_1 = RT \ln P_2/P_1} \text{—— (4) For ideal gas.}$$

~~$\therefore RT \ln f_2/P_2 = \int_0^{P_2} (V - RT/p) dP$~~

~~$\boxed{\therefore RT \ln f/P = \int_0^{P} (V - RT/P) dP}$ ——~~

If f_1 & f_2 are the fugacity of the gas at P_1 & P_2 resply, then eqn ④ will be

$$G_2 - G_1 = RT \ln f_2/f_1 \quad \text{— ⑤}$$

Now we have $G_2 - G_1 = \int_{P_1}^{P_2} v\, dP$ — ⑥

If we add & subtract the quantity $\frac{RT}{P}$ in eq^n ⑥ then

$$G_2 - G_1 = \int_{P_1}^{P_2} \left[\frac{RT}{P} + \left(V - \frac{RT}{P}\right)\right] dp$$

$$= \int_{P_1}^{P_2} \frac{RT}{P} dp + \int_{P_1}^{P_2} \left(V - \frac{RT}{P}\right) dp$$

$$G_2 - G_1 = RT \ln \frac{P_2}{P_1} + \int_{P_1}^{P_2} \left(V - \frac{RT}{P}\right) dp \text{ —— ⑦}$$

Comparing eq^n ⑦ with ⑤, we have

$$RT \ln \frac{f_2}{f_1} = RT \ln \frac{P_2}{P_1} + \int_{P_1}^{P_2} \left(V - \frac{RT}{P}\right) dp \quad \text{or}$$

$$RT \ln \frac{f_2}{f_1} - RT \ln \frac{P_2}{P_1} = \int_{P_1}^{P_2} \left(V - \frac{RT}{P}\right) dp$$

$$RT \ln \frac{f_2/f_1}{P_2/P_1} = \int_{P_1}^{P_2} \left(V - \frac{RT}{P}\right) dp$$

$$RT \ln \frac{f_2/P_2}{f_1/P_1} = \int_{P_1}^{P_2} \left(V - \frac{RT}{P}\right) dp$$

Since all gases becomes ideal as $P \to 0$ ∴ $\frac{f}{P} \to 1$ as $P \to 0$

The ratio f_1/P_1 becomes unity when $P_1 \to 0$

$$\therefore RT \ln f_2/P_2 = \int_0^{P_2} (V - RT/p)\, dp$$

If p & f are written instead of P_2 & f_2 then,

$$\boxed{\therefore RT \ln f/p = \int_0^{P} (V - RT/p)\, dP} \text{ —— (7).}$$

This equation shows that for ideal gas fugacity is proportional to pressure.

Eq^n (4) can be solved from vireal co-efficients of a gas at given pressure and temperature.

$$\boxed{\therefore \ln f/p = B_p P + \frac{1}{2} C_p P^2 + \frac{1}{3} D_p P^3 + \cdots} \text{ —— ⑧}$$

where B_p, C_p, D_p are the vireal coefficients of the gas.

<u>Example</u> : Calculate the fugacity of methane gas at 200 bar and 25°c. The viral coefficient for methane gas at 25°c are as under.

$B_p = -0.001727 \text{ bar}^{-1}$

$C_p = 0.438 \times 10^{-6} \text{ bar}^{-2}$

$D_p = 17 \times 10^{-9} \text{ bar}^{-3}$

<u>Ans</u> :- $\ln f/p = B_p P + 1/2\, C_p P^2 + 1/3\, D_p P^3 + \text{----}$

Given : $B_p = -0.001727 \text{ bar}^{-1}$

$C_p = 0.438 \times 10^{-6} \text{ bar}^{-2}$

$D_p = 17 \times 10^{-9} \text{ bar}^{-3}$

$p = 200 \text{ bar}$.

$\therefore \ln f/p = (-0.001727)(200) + 1/2\,(0.438 \times 10^{-6})(200)^2 + 1/3\,(17 \times 10^{-9})(200)^3$

$\therefore \ln f/p = -0.3454 + \frac{0.01752}{2} + \frac{0.136}{3}$

$\therefore \ln f/p = -0.3454 + 0.00876 + 0.04533$

$\therefore \ln f/p = -0.293$

$\therefore f/p = \text{Inv. } \ln [-0.2913]$

$\therefore f/p = 0.74728$

$\therefore f = 0.74728 \times p$ $\quad [\because p = 200 \text{ bar}]$

$\therefore f = 0.74728 \times 200$

$$\boxed{\therefore f = 149.45 \text{ bar}}$$

<u>Example</u> :- Calculate the fugacity of methane gas at 100 bar at 100°c. The viral coefficients are,

$B_p = -0.677 \times 10^{-3} \text{ bar}^{-1}$; $C_p = 1.447 \times 10^{-6} \text{ bar}^{-2}$

$D_p = 4.1 \times 10^{-9} \text{ bar}^{-3}$

Ans : $\ln f/p = B_p P + \frac{1}{2} C_p P^2 + \frac{1}{3} D_p P^3$

$\therefore \ln f/p = -(0.677 \times 10^{-3} \times 100) + \frac{1}{2}(1.447 \times 10^{-6} \times 10^4) + \frac{1}{3}(4.1 \times 10^{-9} \times 10^6).$

$\therefore \ln f/p = -0.0677 + \frac{0.01447}{2} + \frac{4.1 \times 10^{-3}}{3}$

$\therefore \ln f/p = -0.0677 + 7.235 \times 10^{-3} + 1.3667 \times 10^{-3}$

$\therefore \ln f/p = -0.0590$

$\therefore f/p = \text{Inv. ln}\,[-0.0590]$

$\therefore f/p = 0.9427$

$\therefore f = 0.9427 \times p$ $\quad [\because p = 100\,\text{bar}]$.

$\therefore f = 0.9427 \times 100$

$\boxed{\therefore f = 94.27\,\text{bar}}$

Example :- Calculate (ΔG) change in free-energy when methane gas expands from 10 bar to 1 bar at 46°C. The gas is assumed to be ideal.

Given: $\int_0^p (V - RT/p)\,dp = -0.41$

Ans :- $RT \ln f/p = \int_0^p [V - RT/p]\,dp$

$\therefore \ln f/p = \int_0^p [V - RT/p]\,dP/RT$

where, $R = 8.314$ cal/deg.mole. $\quad p = 10$ bar.

$T = -46°C = 273 - 46 = 227°K$

$\therefore \ln f/p = \frac{-0.41}{8.314 \times 227}$

$\therefore \ln f/p = -2.172 \times 10^{-4}$

$\therefore f/p = \text{Inv. } \ln[-2.172 \times 10^{-4}]$

$\therefore f/p = 0.99978$

$\therefore f = 0.99978 \times P$

$\therefore f = 0.99978 \times 10$

$\boxed{\therefore f = 9.9978}$

Now,

$\Delta G = RT \ln f_2/f_1$

$\therefore \Delta G = 8.314 \times 227 \times \ln \frac{1}{9.9978}$ where $f_1 = 1$. $f_2 = 9.9978$

$\therefore \Delta G = 8.314 \times 227 \times (-4.345)$

$\boxed{\therefore \Delta G = -4345.0 \text{ J/K}}$

* Fugacity and the law of corresponding state :-

For gases, the equation of state is not available for molar volume measurements have not been made, then the law of corresponding states can be used to estimate the fugacity at various temperature and pressures.

$\therefore Z = \frac{PV}{RT}$ where Z is compressibility factor.

$\therefore V = \frac{ZRT}{P}$ —— (I).

Now,

$$RT \ln f/p = \int_0^P [V - RT/p]\, dp$$

Substitute the value of V in above equation, we get,

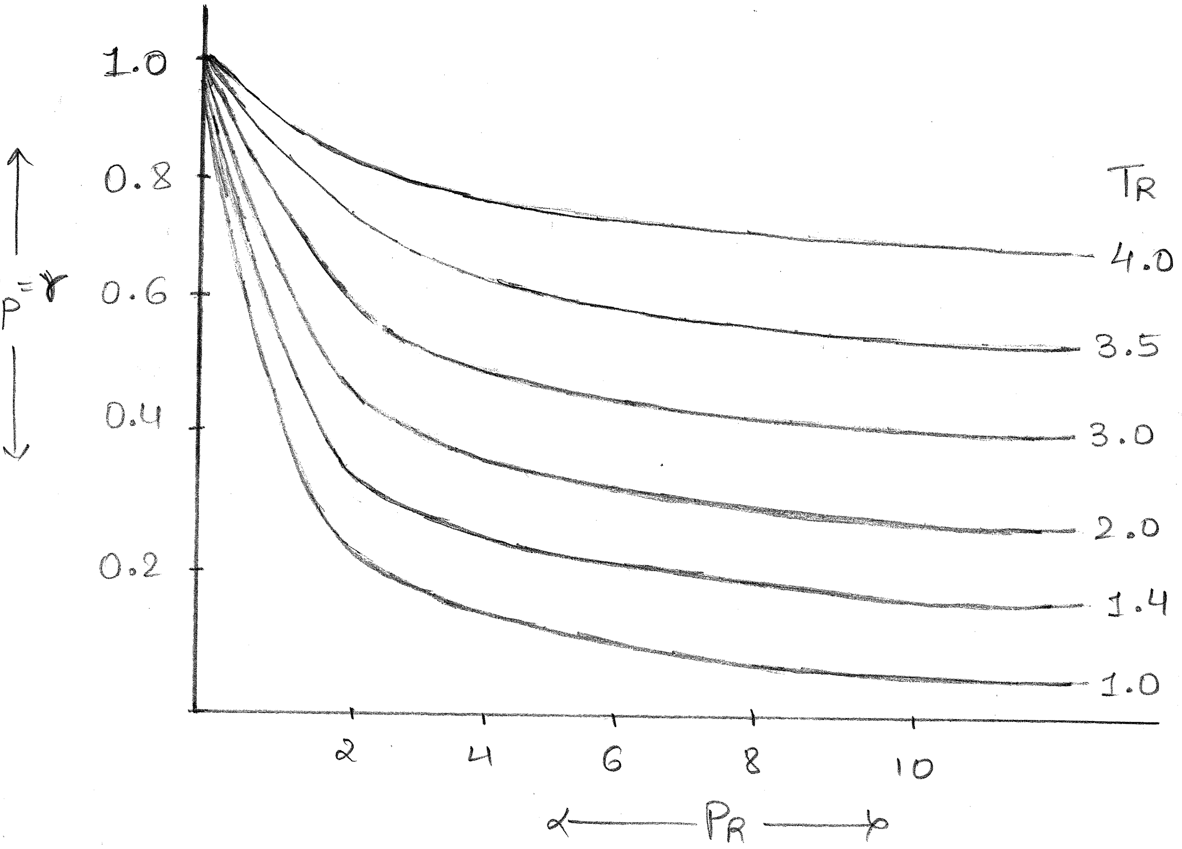
$$\therefore RT \ln f/p = \int_0^P \left[\frac{RT}{P} Z - \frac{RT}{P}\right] dP$$

$$\therefore \cancel{RT} \ln f/p = \cancel{RT} \int_0^P [Z-1]\, dP/P$$

$$\therefore \ln f/p = \int_0^p [z-1]\,dp/p$$

$$\boxed{\therefore \ln f/p = \int_0^p [z-1]\,dP_R/P_R}$$

where P_R is reduced pressure.



It is known that the compressibility factor of all the gases are approximately equal to a given reduced temperature (T_R) and pressure (P_R). The graph shows that at zero reduced pressure, the activity coefficients becomes unity and it may increase or decrease at different value of T_R.

* Molecular basis of third law of thermodynamics:-

In majority of cases, the entropies obtained by statistical method are in arrangement with those obtained in 3rd law of thermodynamics. There are some cases in which some differences has been obtained in CO, NO, N_2O, H^+, H_2O and organic compounds.

The 3^{rd} law values obtained for ~~enthalpy~~ entropy of 1 mole CO at 1 bar and 290°K is 193.3 $JK^{-1}mole^{-1}$. This value is lower than the statistical value of 147.6 $JK^{-1}mole^{-1}$. Similar differences had found for NO and N_2O. In case of H_2O, the stastistical value is higher than 3^{rd} law value by 3.3 $JK^{-1}mole^{-1}$. This difference is due to failure of material to form perfect crystalline state at absolute zero for 3^{rd} law to be applied.

It is perfectly ordered state of crystal with all molecules in some lowest energy state which is molecular basis of 3^{rd} law which states that entropy is zero at absolute zero. In case of CO, the entropy of absolute zero is 4.3 $JK^{-1}mole^{-1}$. A disordered pattern like CO-CO-CO-CO-CO-CO-CO----- is expected for such a molecule.