ENTROPY OF A PERFECT GAS : GIBB'S PARADOX

The entropy of a perfect gas is as follows

$$S = \left(NK \ln Z + \frac{3}{2} NK \right) \quad — (1)$$

Where the partition function (Z) of a perfect gas is given by,

$$Z = \frac{V}{h^3} \left(2\pi m KT \right)^{3/2} \quad — (2)$$

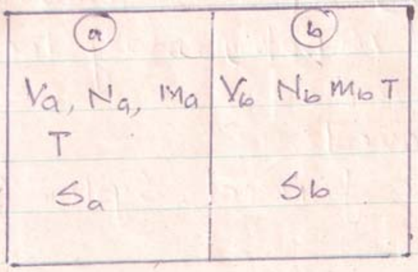
From eq^n (1) and (2):

$$S = \left[NK \ln \left\{ \frac{V}{h^3} \left(2\pi m KT \right)^{3/2} \right\} + \frac{3}{2} NK \right] \quad — (3)$$

Eq^n (3) may also be written as

$$S = NK\left\{ \ln V + \frac{3}{2}\ln m + \frac{3}{2}\ln T + C \right\} \quad \text{--- (4)}$$

Where C is a constant involving the other two constant h & K.



Consider two systems (a) and (b) partitioned by a barrier as shown in fig. According to eq^n (4) we have the following two eq^n

$$\left.\begin{aligned} S_a &= N_a K\left\{ \ln V_a + \frac{3}{2}\ln m_a + \frac{3}{2}\ln T + C \right\} \\ S_b &= N_b K\left\{ \ln V_b + \frac{3}{2}\ln m_b + \frac{3}{2}\ln T + C \right\} \end{aligned}\right\} \quad \text{--- (5)}$$

Where N = Total no. of particles.
m = mass of particle
& V = volume of system.

Assuming the additive property of entropy and removing the barrier the entropy of the joint system would be

$$S_{ab} = S_a + S_b = \left[N_a K\left\{ \ln V_a + \frac{3}{2}\ln m_a + \frac{3}{2}\ln T + C \right\} + N_b K\left\{ \ln V_b + \frac{3}{2}\ln m_b + \frac{3}{2}\ln T + C \right\} \right] \quad \text{--- (6)}$$

Now, If the particles of the two systems are the same and for conviniency $V_a = V_b = V$ and $N_a = N_b = N$, the entropy of each of the individual system would be

$$S = S_a = S_b = NK\left\{\ln V + \frac{3}{2}\ln m + \frac{3}{2}\ln T + c\right\} \quad \text{--- (7)}$$

Then the entropy of the combined system would be

$$S_{ab} = S_a + S_b = 2NK\left\{\ln V + \frac{3}{2}\ln m + \frac{3}{2}\ln T + c\right\} \quad \text{--- (8)}$$

Now, The actual entropy of the combined system using eq^n (4) for entropy may be determined.

Let the partition be removed

Then the entropy of the joined System (ab) is given by:

$$S_{ab} = 2NK\left\{\ln 2V + \frac{3}{2}\ln m + \frac{3}{2}\ln T + c\right\}$$

ie $$S_{ab} = \left[2NK\left\{\ln V + \frac{3}{2}\ln m + \frac{3}{2}\ln T + c\right\}\right.$$

$$+ 2NK\ln 2$$

$$\therefore \quad S_{ab} = S_a + S_b + 2NK\ln 2 \quad \text{--- (9)}$$

Eq^n (8) and (9) are observed to be different.

This indicates that by mixing the two different gases each containing same no. of molecules (N) by removing the partition between them, the entropy of the joined System increases by an unaccountable amount $2NK\ln 2$. This additional entropy is called "Entropy of Mixing"

This peculiar behaviour of the entropy is called "Gibb's PARADOX.

Resolution of the PARADOX (By Gibbs'):

Consider the two Systems as same so

that the gas molecules become identical and indistinguishable. Then the weight of the configuration is given by

$$W = \prod \frac{g_i^{n_i}}{n_i!}$$

and not $W = \lfloor n \prod \frac{g_i^{n_i}}{n_i!}$

This leads to the following expression for the entropy of a perfect gas.

$$S = \left[NK \ln \left\{ \left(\frac{V}{N}\right) \left(\frac{2\pi mKT}{h^2}\right)^{3/2} \right\} + \frac{5}{2} NK \right] \quad \text{(10)}$$

The entropy of the combined system is obtained by putting 2N for N and 2V for V. Thus from eq^n (10) we get

$$S_{ab} = 2\left[NK \ln \left\{ \left(\frac{V}{N}\right) \left(\frac{2\pi mKT}{h^2}\right)^{3/2} \right\} + \frac{5}{2} NK \right] \quad \text{(11)}$$

Comparing eq^n (10) and (11) we find that

$$S_{ab} = 2S = S_a + S_b$$

Thus the paradox is resolved. There is no extra term. To resolve the paradox the property of indistinguishability of particles (a quantum property) has been used.