Entropy of Mixing – Gibb's Paradox

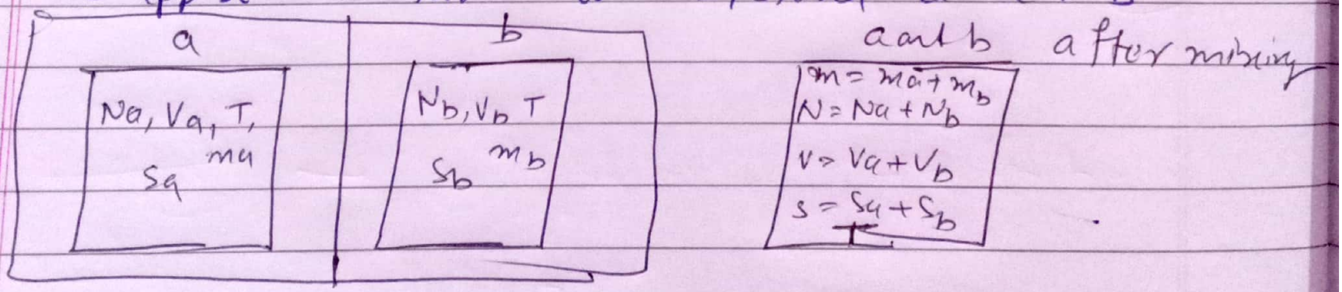
Entropy of mixing

In this topic we take two system and add this system when we saw the result the addition of this system new system has different entropy But the entropy is has a extensive property (means additive property) the addition of two system result is not confirmed the extensive property this result is observed or calculated by Gibb's which shows a paradoxial result show this is called a Gibb's Paradox.

This Gibb's paradox is removed by quantum theory.

[So we find hear a Gibb's Paradox equation and it resolved equation]

Suppose we take two system a and b



Entropy of system a and b can be written as

$$S_a = N_a k \left[\log V_a + \frac{3}{2} \log m_a + \frac{3}{2} \log T + C \right] \quad -(1)$$

$$S_b = N_b k \left[\log V_b + \frac{3}{2} \log m_b + \frac{3}{2} \log T + C \right] \quad -(2)$$

Partition function of a perfect gas is

$$Z = \frac{V}{h^3}(2\pi mkT)^{3/2}$$

the entropy of a perfect gas is

$$S = Nk \log Z + \frac{3}{2}Nk$$

$$S = Nk \log\left[\frac{V}{h^3}(2\pi mkT)^{3/2}\right] + \frac{3}{2}Nk$$

or

$$S = Nk\left[\log V + \frac{3}{2}\log m + \frac{3}{2}\log T + C\right]$$

The entropy of joint system have been given by

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

if the particles of the two system are the same and we can write as

$V_a = V_b = V$, $N_a = N_b = N$ so the individual system would be

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$$S_a = S_b = Nk\left[\log V + \frac{3}{2}\log m + \frac{3}{2}\log T + C\right] \quad \text{--- (4)}$$

Then using the additive property of entropy of combined system would be written as

$$S_{ab} = S_a + S_b = 2NK\left[\log V + \frac{3}{2}\log m + \frac{3}{2}\log T + C\right] \quad \text{--- (5)}$$

but using eqn no. (3) the combined system has 2N particle & 2V volume so the actual entropy is written as

$$S_{ab} = 2NK\left[\log 2V + \frac{3}{2}\log m + \frac{3}{2}\log T + C\right]$$

$$= 2NK\left[\log V + \frac{3}{2}\log m + \frac{3}{2}\log T + C\right] + 2NK\log 2$$

$$\boxed{S_{ab} = S_a + S_b + 2NK\log 2} \quad \text{--- (6)}$$

~~eqn (5) and~~ (6) showing and extra factor $2NK\log 2$ which shows mixing of two different gases each containing same number of molecules N. The entropy of joint system increases by an unaccountable amount $2NK\log 2$. This additional entropy is called the entropy of mixing : This is showing a paradoxial result. This peculiar behaviour of the entropy is called Gibb's paradox

Resolving of Gibb's Paradox

[When we first take entropy mixing here we take distinguishable particle but resolving the gibb's paradox we take quantum theory where we use particles are completely indistinguishable and hence have introduced the factor $\frac{1}{N!}$ in the definition of entropy.

so

$$S = NK \log\left[\frac{V}{h^3}\frac{(2\pi mKT)^{3/2}}{N!}\right] + \frac{3}{2}NK$$

[here we applying sterling formula]

$$\boxed{S = NK\log\left[\left(\frac{V}{N}\right)\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\right] + \frac{5}{2}NK} \quad (7)$$

replacing N by 2N and V by 2V

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

$$= 2\left[NK\log\left\{\left(\frac{V}{N}\right)\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\right\} + \frac{5}{2}NK\right] \quad (8)$$

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

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