MAXWELL - BOLTZMANN DISTRIBUTION LAW! —

In Maxwell-Boltzmann distribution law, the particles are distinguishable.

let N particles in different cells, the N particles can be put in N! ways. assume that the ith cell are n_i particles in g_i different levels. The first particles can occupy g_i levels in g_i different ways, the second particle in g_i ways, the ~~n_i particles~~ can third l particles in g_i ways and so on.

Therefore, in $(g_i)^{n_i}$ ways, the n_i particles can occupy g_i levels. The arrangements among n_i identical particles do not create new microstates and n_i particles can be distibuted in $n_i!$ ways. so, if there are K no. of groups, then the total no. of microstates is

$$\Omega\{g_i, n_i\} = N! \prod_{i=1}^{K} \frac{(g_i)^{n_i}}{n_i!} \quad \text{——— (1)}$$

Thus, $\Omega\{g_i, n_i\}$ denotes the no. of microstates for distinguishable particles. The g_i different ways is called the degeneracy in the ith cell.

We know that the total No. of particles is constant and for isolated system the total energy U is also constant.

Thus,

$$N = \sum_i n_i = \text{constant} \quad \text{——— (2)}$$

$$\text{and } U = \sum_i n_i \epsilon_i = \text{constant} \quad \text{——— (3)}$$

Where ϵ_i is the energy of the ith particles.

The Most probable distribution (Maximum $\Omega(n_i, g_i)$ with respect to n_i)

$$\ln \Omega\{g_i, n_i\} = \ln N! + \sum n_i \ln g_i - \sum \ln n_i!$$

$$= N \ln N - N + \sum n_i \ln g_i - \sum n_i \ln n_i + \sum n_i \quad \text{--- (4)}$$

(from stirling approximation, $\ln x! \simeq x \ln x - x$)

We maximize $\Omega\{g_i, n_i\}$ with respect to n_i subject to the conditions.

$$\delta N = \sum_i \delta n_i = 0 \quad \text{--- (5)}$$

and $$\delta U = \sum_i \epsilon_i \delta n_i = 0 \quad \text{--- (6)}$$

$$\therefore \delta(\ln \Omega) = \sum_i (\ln g_i - \ln n_i)\, \delta n_i \quad \text{--- (7)}$$

we introduce two Langrage's undetermined multipliers α and β, such that

$$\sum_i \left[\ln g_i - \ln n_i - (\alpha + \beta \epsilon_i)\right] \delta n_i = 0 \quad \text{--- (8)}$$

Since, δn_i is arbitrary, we have

$$\ln\left(\frac{g_i}{n_i}\right) = (\alpha + \beta \epsilon_i)$$

or, $$\bar{n}_i = g_i \cdot e^{-(\alpha + \beta \epsilon_i)} \quad \text{--- (9)}$$

Therefore, the no. of particles per state the average occupation no.

$$\boxed{f(\epsilon_i) = \frac{n_i}{g_i} = e^{-(\alpha + \beta \epsilon_i)}} \quad \text{--- (10)}$$

This is called Maxwell-Botzmann distribution function.

The Constant α is determined by the normalised Condition in terms of β as

$$N = \sum_i \bar{n}_i = \sum_i g_i \cdot e^{-(\alpha + \beta \epsilon_i)} \quad \text{——— (11)}$$

or, $$N e^{\alpha} = \sum_i g_i \cdot e^{-\beta \epsilon_i}$$

we replace summation by integration, where g_i is the density of states is given by

$$g(p)\,dp = \frac{4\pi V p^2 dp}{h^3}$$

$$\therefore N e^{\alpha} = \frac{4\pi V}{h^3} \int_0^{\infty} p^2 dp\, e^{-\frac{\beta p^2}{2m}} = \frac{V}{\lambda^3} \quad \text{——— (12)}$$

where $\lambda = \sqrt{\frac{h^2 \beta}{2\pi m}}$

We can determine β from the requirement of an ideal gas

$$U = \sum \epsilon_i \bar{n}_i = e^{-\alpha} \sum \epsilon_i g_i e^{-\beta \epsilon_i}$$

$$= \frac{3}{2} N K_B T \quad \text{——— (13)}$$

$$\therefore e^{-\alpha} \frac{V}{h^3} \int_0^{\infty} \left(\frac{p^2}{2m}\right) 4\pi p^2 e^{-\frac{\beta p^2}{2m}} dp = \frac{3}{2} N K_B T$$

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or, $$N \left(\frac{h^2 \beta}{2\pi m}\right)^{3/2} \frac{1}{h^3} \left(\frac{2\pi}{m}\right) \int_0^{\infty} p^4 e^{-\beta p^2/2m} dp = \frac{3}{2} N K_B T$$

we put $\sqrt{\frac{\beta}{2m}} \cdot p = x$

$$\therefore dp = \sqrt{\frac{2m}{\beta}} \cdot dx$$

$$\therefore \left(\frac{\beta}{2\pi m}\right)^{3/2}\left(\frac{2\pi}{m}\right)\left(\sqrt{\left(\frac{2m}{\beta}\right)}\right)^{4}\sqrt{\frac{2m}{\beta}}\int_0^\infty x^4 e^{-x^2}\,d.x = \frac{3}{2}K_BT$$

We, get
$$\left(\frac{\beta}{2\pi m}\right)^{3/2}\cdot\left(\frac{2\pi}{m}\right)\left(\frac{2\pi}{m}\right)^{9/2}\cdot\frac{1}{2}\Gamma\left(\frac{5}{2}\right) = \frac{3}{2}K_BT$$

$$\therefore \frac{1}{\beta} = K_BT \quad \text{or,} \quad \boxed{\beta = \frac{1}{K_BT}}$$

$$\therefore Ne^{\alpha} = \frac{V}{\lambda^3}$$

where $\lambda = \left(\frac{h^2}{2\pi m K_BT}\right)^{1/2}$ ——— (14)

Entropy of ideal Boltzmann Gas :-

The entropy of Botzmann gas is given by Boltzmann relation.

$$S = K_B \ln \Omega\{g_i, n_i\} \quad \text{——— (15)}$$

$$= K_B\left[N\ln N + \sum_i \bar{n}_i \ln\left(\frac{g_i}{n_i}\right)\right]$$

$$= K_B\left[N\ln N + \sum_i \bar{n}_i(\alpha + \beta\epsilon_i)\right]$$

$$= K_B\left[N\ln N - N\ln A + \frac{U}{K_BT}\right], \left\{\text{where } A = e^{\alpha}, \; \& \; N = \sum \bar{n}_0\right\}$$

$$= \sum g_i e^{-(\alpha+\beta\epsilon_i)}$$

$$= A\sum g_i e^{-\beta\epsilon_i}$$

$$\therefore \ln N = \ln A + \ln \sum g_i e^{-\beta\epsilon_i} \quad \text{——— (16)}$$

$$\therefore S = NK_B \ln \sum g_i e^{-\beta \varepsilon_i} + \frac{U}{T}$$

We can derive the ideal gas equation in the following ways :-

$$S = K_B \left[N\ln N - N\ln A + \frac{U}{K_B T} \right] \quad \text{--- (17)}$$

where, $A = e^{-\alpha} = \frac{V}{N\lambda^3} = \left(\frac{V}{N}\right)\left(\frac{2\pi m K_B T}{h^2}\right)^{\frac{1}{2}}$

$$\therefore S = K_B \left[N\ln N + N\ln V - N\ln N + N\ln\left(\frac{2\pi m K_B T}{h^2}\right) + \frac{U}{K_B T} \right]$$

$$= K_B \left[N\ln V + N\ln\left(\frac{2\pi m K_B T}{h^2}\right) + \frac{U}{K_B T} \right] \quad \text{--- (18)}$$

from Ist law of thermodynamics

$$dU = Tds - pdv \quad \text{--- (19)}$$

$$\therefore P = T\left(\frac{\partial s}{\partial V}\right)_U = \frac{NK_B T}{V} \quad \text{--- (20)}$$

or, $PV = NK_B T$ which is the ideal gas equation.

The relation,

$$\boxed{S = NK_B \left[\ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln\left(\frac{2\pi m K_B}{h^2}\right) - \ln N + \frac{5}{2} \right]} \quad \text{--- (21)}$$

This equation is called Sackur-Tetrode equation.

This equation was experimentally varified as the correct entropy of an ideal gas at high temperatures.

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