

PARTITION FUNCTION :-

We introduce the partition function as

$$Z_{sp} = \sum_i e^{-\epsilon_i/k_B T} \quad \text{--- (1)}$$

for a single particle which states for the German word Zustandssumme meaning "sum over states".

The partition function defined as Z_{sp} is independent of the total no. of particles.

The partition function is ~~statistical~~ extremely important in statistical mechanics as it is clear from the following discussions :-

Partition function of a monochromatic ideal gas :-

We define the partition function for a single particles as

$$Z_{sp} = \sum_i g_i e^{-\frac{\epsilon_i}{k_B T}}$$

We assume that the particles are distinguishable, thus, the energy

$$U = \sum A g_i \epsilon_i e^{-\frac{\epsilon_i}{k_B T}} \quad \text{--- (1)}$$

whose the constant A is given by

$$N = \sum_i A g_i e^{-\frac{\epsilon_i}{k_B T}}$$

$$\text{Thus, } U = N \frac{\sum_i g_i \epsilon_i e^{-\frac{\epsilon_i}{k_B T}}}{\sum_i g_i e^{-\frac{\epsilon_i}{k_B T}}}$$

$$= N K_B T \frac{\partial}{\partial T} \ln \left(\sum_i g_i e^{-\frac{\epsilon_i}{K_B T}} \right)$$

$$= N K_B T^2 \frac{\partial}{\partial T} \ln (Z_{sp})$$

The entropy of the monochromatic ideal gas is

$$S = K_B \ln \Omega \{ g_i, n_i \} \quad \text{--- (2)}$$

For distinguishable particles,

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

$$\therefore S = K_B \ln \left[N! + \sum_i n_i \ln g_i - \ln n_i! \right] \quad \text{--- (3)}$$

Using Stirling approximation, we get

$$\ln n_i! = n_i \ln n_i - n_i$$

$$\therefore S = K_B \sum_i n_i \ln g_i - n_i \ln n_i + n_i + K_B \ln N!$$

$$= K_B \left\{ \sum_i n_i \ln \left(\frac{g_i}{n_i} \right) + N \right\} + K_B \ln N!$$

$$= K_B \left[\sum_i n_i \left(-\ln A + \frac{\epsilon_i}{K_B T} \right) + N \right] + K_B \ln N! \quad \text{--- (4)}$$

Again, $N = A \sum g_i e^{-\frac{\epsilon_i}{K_B T}}$

$$= A Z_{sp}$$

$$\therefore \ln A = \ln N - \ln Z_{SP}$$

$$\begin{aligned} \therefore S &= K_B \left[-N \ln N + N \ln Z_{SP} + \frac{U}{K_B T} + N \right] \\ &= N K_B \ln Z_{SP} + N K_B T \frac{\partial}{\partial T} \ln(Z_{SP}) \quad \text{--- (5)} \end{aligned}$$

Now, for monoatomic gas, we can write,

$$\begin{aligned} Z_{SP} &= \sum_i g_i e^{-\frac{\epsilon_i}{K_B T}} = \int_0^{\infty} g(\epsilon) e^{-\frac{\epsilon}{K_B T}} d\epsilon \\ &= \frac{2\pi V}{h^3} (2\pi m)^{3/2} \int_0^{\infty} e^{1/2} e^{-\frac{\epsilon}{K_B T}} d\epsilon \end{aligned}$$

We put, $\frac{\epsilon}{K_B T} = x$

∴, $d\epsilon = K_B T dx$

$$\begin{aligned} \therefore Z_{SP} &= \frac{2\pi V}{h^3} (2\pi m)^{3/2} \cdot (K_B T)^{3/2} \int_0^{\infty} x^{1/2} e^{-x} dx \\ &= \frac{2\pi V}{h^3} (2\pi m K_B T)^{3/2} \cdot \Gamma(3/2) \\ &= V \left(\frac{2\pi m K_B T}{h^2} \right)^{3/2} \quad \text{--- (6)} \end{aligned}$$

Thus the internal energy (U) = $N K_B T^2 \frac{\partial}{\partial T} (\ln Z_{SP})$

$$\ln Z_{SP} = \ln V + 3/2 \ln \left(\frac{2\pi m K_B}{h^2} \right) + \frac{3}{2} \ln T$$

$$\therefore \frac{\partial}{\partial T} \ln(Z_{SP}) = \frac{3}{2} \cdot \frac{1}{T}$$

Thus, $U = N K_B T^2 \cdot \frac{3}{2} \cdot \frac{1}{T}$

$$U = \frac{3}{2} N K_B T \quad \text{--- (7)}$$

The heat capacity due to translation is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} N K_B = \frac{3}{2} R \text{ per mole} \quad \text{--- (8)}$$

We can obtain, the thermodynamic parameters for the monoatomic gas from the partition function using the thermodynamic relations.

The Thermodynamic relations are

$$dF = -SdT - PdV \quad \text{--- (9)}$$

Where F is the Helmholtz free energy

The pressure (P) is

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

$$\begin{aligned} \text{we have, } F = U - TS &= N K_B T^2 \frac{\partial}{\partial T} \ln(Z_{sp}) - N K_B T \ln Z_{sp} - \\ & N K_B T^2 \frac{\partial}{\partial T} \ln(Z_{sp}) \\ &= - N K_B T \ln Z_{sp} \quad \text{--- (10)} \end{aligned}$$

$$\therefore P = N K_B T \frac{\partial}{\partial V} \ln(Z_{sp}) \quad \text{--- (11)}$$

$$\text{Now, } \ln(Z_{sp}) = \ln V + \frac{3}{2} \ln \left(\frac{2\pi m K_B}{h^2} \right) + \frac{3}{2} \ln T$$

$$\therefore \frac{\partial}{\partial V} \ln(Z_{sp}) = \frac{1}{V}$$

$$\therefore P = N K_B T \cdot \frac{1}{V}$$

$$\text{or, } \boxed{PV = N K_B T} \quad \text{--- (12)}$$

This is ideal gas equation.

$$\text{The entropy } S = - \left(\frac{\partial F}{\partial T} \right)_V$$

$$= N K_B \ln Z_{SP} + N K_B T \frac{\partial}{\partial T} \ln(Z_{SP})$$

$$= N K_B T \cdot \frac{3}{2} \cdot \frac{1}{T} + N K_B \left[\ln V + \frac{3}{2} \ln \left(\frac{2 \pi m K_B}{h^2} \right) + \frac{3}{2} \ln T \right]$$

$$S = N K_B \left[\ln V + \frac{3}{2} \ln \left(\frac{2 \pi m K_B}{h^2} \right) + \frac{3}{2} \ln T + \frac{3}{2} \right] \quad \text{--- (13)}$$

This is known as Sackur-Tetrode equation.

For an isobaric process, $\Delta S = 0$

$$\text{Thus, } \ln V_1 + \frac{3}{2} \ln T_1 = \ln V_2 + \frac{3}{2} \ln T_2$$

$$\text{i.e. } V T^{3/2} = \text{Constant} \quad \text{--- (14)}$$

Using ideal gas equation, $PV = N K_B T$, one gets

$$P V^{5/3} = \text{Constant for adiabatic process}$$

For adiabatic process we have

$$P V^\gamma = \text{Constant}$$

$$\gamma = \frac{5}{3} = 1 + \frac{2}{f}$$

$\therefore f = 3$ is the D.F., consistent with the degree of freedom (D.F) for, monoatomic gas.

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