

Molecular partition function

* Helmholtz free energy & partition function

We know that

$$A = E - TS$$

Putting the value of E as we get.

$$A = kT^2 \left(\frac{\partial \ln \Omega}{\partial T} \right)_V - T \left[kT \left(\frac{\partial \ln \Omega}{\partial T} \right)_V + k \ln \Omega \right]$$

$$A = kT^2 \left(\frac{\partial \ln \Omega}{\partial T} \right)_V - kT^2 \left(\frac{\partial \ln \Omega}{\partial T} \right)_V - kT \ln \Omega$$

$$A = -kT \ln \Omega$$

* Enthalpy & partition function

Since,

$$H = E + PV$$

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

$$\therefore H = kT^2 \left(\frac{\partial \ln \Omega}{\partial T} \right)_V + kT \left(\frac{\partial \ln \Omega}{\partial V} \right)_T \cdot V$$

$$\text{or } H = kT \left[T \left(\frac{\partial \ln \Omega}{\partial T} \right)_V + V \left(\frac{\partial \ln \Omega}{\partial V} \right)_T \right]$$

* Gibbs free energy & partition function

Since,

$$G = H - TS$$

$$G = E + PV - TS$$

$$G = A + PV$$

$$H = E + PV$$

$$A = E - TS$$

$$\therefore G = -KT \ln \theta + KT \left(\frac{\partial \ln \theta}{\partial V} \right)_T \cdot V$$

$$\text{or } G = KT \left[V \left(\frac{\partial \ln \theta}{\partial V} \right)_T - \ln \theta \right]$$

* Translational Partition Function

On solving the schrodinger wave equation for particles in one dimensional box. The translational energy value is calculated as:

$$E_t = \frac{n^2 h^2}{8ma^2}$$

Since, degree of degeneracy $g_i = 1$

Thus, Partition function —

$$q_t = \sum \exp\left(-\frac{E_i}{KT}\right)$$

$$\therefore q_t = \sum_{g_i=1} \exp\left[\left(\frac{-n^2 h^2}{8ma^2}\right) \times \frac{1}{KT}\right]$$

Since, Energy levels are closely spaced. \therefore the summation can be replaced by integration —

$$\therefore (q_t)_x = \int_0^{\infty} \exp\left(\frac{-n^2 h^2}{8ma^2} \times \frac{1}{KT}\right) dx$$

Where, $(q_t)_x$ is the translational partition function in x -direction.

as solving this —

$$(q_t)_x = \frac{(2\pi m kT)^{1/2}}{h} \cdot a$$

similarly,

$$(q_t)_y = \frac{(2\pi m kT)^{1/2}}{h} \cdot b$$

$$\text{and } (q_t)_z = \frac{(2\pi m kT)^{1/2}}{h} \cdot c$$

In three dimensional case, translational partition function is —

$$q_t = (q_t)_x \cdot (q_t)_y \cdot (q_t)_z$$

$$q_t = (2\pi m kT)^{3/2} \times \frac{abc}{h^3}$$

$$q_t = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \cdot V$$

V = volume of the box.

* Translational energy of the gas.

We know that —

$$E = kT^2 \left(\frac{\partial \ln \theta}{\partial T} \right)_V$$

①

$$\theta = \frac{q^N}{N!}$$

as differentiating st —

$$\ln \theta = N \ln q - \ln N!$$

using Stirling approximation -

$$\ln \theta = N \ln q - N \ln N + N$$

on differentiating w.r.t T at constant V we get.

$$\left(\frac{\partial \ln \theta}{\partial T} \right)_V = N \left(\frac{\partial \ln q}{\partial T} \right)_V \quad \text{--- (2)}$$

since, $q = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} \cdot V$

or ~~or~~ ~~different~~

$$\ln q = \underbrace{\ln \left(\frac{2\pi m k}{h^2} \right)^{3/2}}_{\text{constant}} + \ln V + \underbrace{3/2 \ln T}_{\text{constant}}$$

diff. w.r.t T at constant V we get.

$$\left(\frac{\partial \ln q}{\partial T} \right)_V = \frac{3}{2} T \quad \text{--- (3)}$$

using eqs - (1), (2) & (3)

$$E = k T^2 \times N \times \frac{3}{2} T$$

$$E = k T \times N \times \frac{3}{2}$$

$$E = \frac{3}{2} RT$$

since,

$$k N = n R$$

$$n = 1$$