Partition function :-

The partition function is defined as:-

$$q = \sum_{i=0}^{i=\infty} g_i \exp\left(-E_i/kT\right)$$

Where, g_i = statistical weight factor and it is equal to the degree of degeneracy.

K = Boltzmann constant and equal to the ratio of gas constant 'R' & the Avogadro's no.

E_i = energy of quantum states in excesses of the lowest possible value.

T = temperature in kelvin scale.

Partition function is a dimensionless quantity depends on the mol. weight, mol. volume & T. It describe how the energy is partitioned (distributed) among the various molecules.

charactristics :-

① It indicates modes of distribution of particles in various energy levels.

② It is a pure no. & hence dimensionless quantity.

③ It cannot have zero value. The lowest value would be 1 at 0K.

④ It is applicable to any physical state of the system.

* Thermodynamic properties in terms of Partition function :-

① Energy and Partition function

Let us consider an ensemble of assemblies N.

The average energy of the system is —

$$E = \frac{\sum N_i E_i}{\sum N_i}$$

(6)

But from Boltzmann distribution law:-

$$N_i = N_0 \exp^{-\epsilon_i/KT}$$

$$\therefore E = \frac{N_0 \sum \epsilon_i e^{-\epsilon_i/KT}}{\sum N_0 e^{-\epsilon_i/KT}} \longrightarrow ①$$

The cannonical ensemble partition function Q. is given by -

$$Q = \sum \exp^{-\epsilon_i/KT}$$

differentiating it w.r.t. T at constant V

$$\left(\frac{\partial Q}{\partial T}\right)_V = \frac{1}{KT^2} \sum \epsilon_i \exp^{-\epsilon_i/KT} \longrightarrow ②$$

$$\text{or } \epsilon_i e^{-\epsilon_i/KT} = KT^2 \left(\frac{\partial Q}{\partial T}\right)_V \longrightarrow ③$$

From eq^s - ①, ② & ③ we get -

$$E = \frac{KT^2 \left(\frac{\partial Q}{\partial T}\right)_V}{Q}$$

$$\boxed{E = KT^2 \left(\frac{\partial \ln Q}{\partial T}\right)_V}$$

② Heat Capicity and Partition Function

Molar heat capacity at constant volume (Cv) defined as the change in internal energy w.r.t. T at constant V.

i.e $$C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad \text{——} ①$$

But $$E = KT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V \quad \text{——} ②$$

∴ $$C_V = \frac{\partial}{\partial T}\left[KT^2\left(\frac{\partial \ln Q}{\partial T}\right)\right]_V$$

$$\boxed{C_V = K\left[2T\left(\frac{\partial \ln Q}{\partial T}\right)_V + T^2\left(\frac{\partial^2 \ln Q}{\partial T^2}\right)_V\right.}$$

③ Entropy & Partition function

We know that –

$$E = f(T, V)$$

on differentiating it ~~w.r.t T at constant~~.

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \quad \text{——} ①$$

From combined eqn. of 1st & 2nd law of thermodynamics.–

$$TdS = dE + PdV. \quad \text{——} ②$$

Putting the value of dE from eqn –① in to eqn –②

$$TdS = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV + PdV$$

or $T ds = \left(\frac{\partial E}{\partial T}\right)_v dT + \left[\left(\frac{\partial E}{\partial v}\right)_T + p\right] dv$

at Constant v —

$dv = 0.$

$\therefore\ T ds = \left(\frac{\partial E}{\partial T}\right)_v dT$

$$\boxed{ds = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_v dT.}$$

on integrating with the limit $T = 0$ to $T = T$,

$$\int_{T=0}^{T=T} ds = \int_{T=0}^{T=T} \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)_v dT$$

Now putting the value of $E = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_v$

and solving we get —

$$\boxed{S = kT\left(\frac{\partial \ln Q}{\partial T}\right)_v + k \ln Q.}$$

Dr. A. K. Gupta
chemistry
(L.S. College)