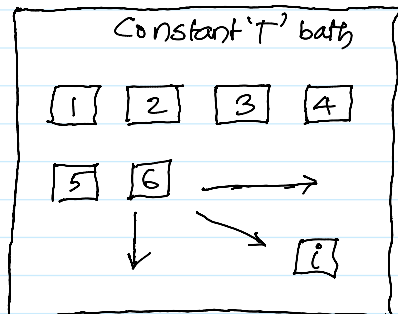


# Canonical Ensemble

Monday, September 28, 2020 10:54 AM

→ Ensemble is defined as large collection of Identical units or replicas of the system. The average value of property of ensemble correspond to time averaged value of corresponding macroscopic property of the system.



(These copies are held fixed in space such that they are distinguishable)

Volume 'V'  
Temperature 'T'  
Particles (N) } constant

Canonical Ensemble.

IF Volume 'V' and energy is fixed, then corresponding ensemble is known as micro canonical ensemble.

In canonical ensemble, each member is embedded in a temperature bath such that ensemble energy is constant.

Walls that define volume of units can conduct heat, allowing for energy exchange.

Total energy of ensemble is given by

$$E_c = \sum_i a_{(c)i} \cdot E_i \quad - (2)$$

$a_{(c)i}$  - Occupation Number corresponding to the number of ensemble members having energy  $E_i$ .

The weight  $w_c$  associated with a specific configuration of energy among the  $N_c$  members of the ensemble is given by

$$w_c = \frac{N_c!}{\prod_i a_{(c)i}!} \quad - (3)$$

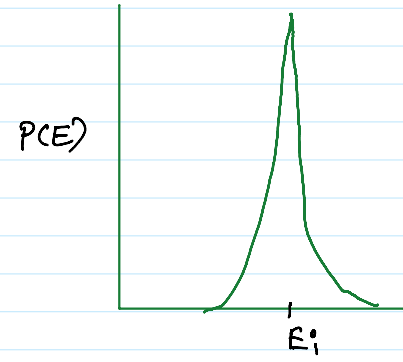
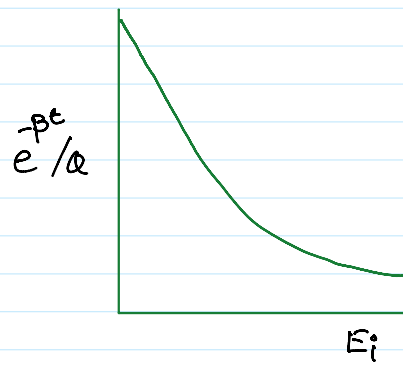
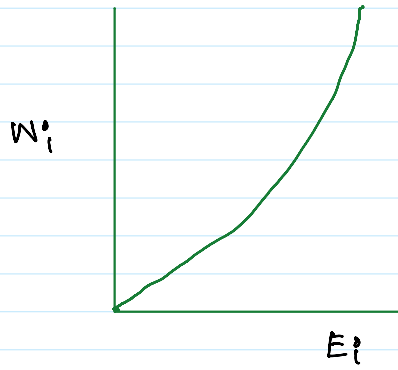
The probability of finding an ensemble unit at energy  $E_i$

$$P(E_i) = \frac{W_i e^{-\beta E_i}}{\mathcal{Q}} \quad - (4)$$

$W_i$  - Number of states present at energy  $E_i$

$$\mathcal{Q} = \sum_i W_i e^{-\beta E_i}$$

$n^c$   
( Canonical Partition Function )

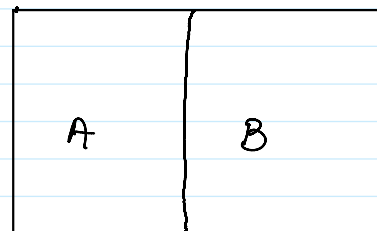




## Relating $Q$ to $q$ for an Ideal Gas

Monday, September 22, 2020 11:36 AM

In relating the canonical partition function  $Q$  to the partition function describing members of the ensemble  $q$  - discussion is restricted to systems consisting of "Independent" Idea of particles in which interaction between particles is negligible.



The relationship between  $Q$  and  $q$  is derived by considering an ensemble made up of two distinguishable units A and B as shown

$$\rightarrow Q = \sum_n e^{-\beta \epsilon_n}$$

$$\rightarrow Q = \sum_n e^{-\beta(\epsilon_{A_n} + \epsilon_{B_n})}$$

$$e^{a+b} = e^a \cdot e^b$$

$\epsilon_{A_n}, \epsilon_{B_n}$  refer to energy levels associated with units A & B resp

$$Q = \sum_n e^{-\beta(\epsilon_{A_n} + \epsilon_{B_n})} = e^{-\beta(\epsilon_{A_0} + \epsilon_{B_0})} + e^{-\beta(\epsilon_{A_1} + \epsilon_{B_1})} + e^{-\beta(\epsilon_{A_2} + \epsilon_{B_2})} + \dots$$

$$\therefore Q = (e^{-\beta \epsilon_{A_0}} + e^{-\beta \epsilon_{A_1}} + e^{-\beta \epsilon_{A_2}} + \dots) \cdot (e^{-\beta \epsilon_{B_0}} + e^{-\beta \epsilon_{B_1}} + e^{-\beta \epsilon_{B_2}} + \dots)$$

$$\therefore Q = (q_A)(q_B)$$

A and B are identical systems  $\therefore q_A = q_B$

$$\therefore Q = q^2 \quad (\text{When ensemble is consisting of '2' units})$$

Extending this result to a system with  $N$  distinguishable units, the canonical partition function is simply the product of unit partition functions

$$Q = q^N$$

### Modification:-

For  $N$  indistinguishable particles we have to divide given relation with  $N!$

$$\therefore Q = \frac{q^N}{N!}$$

For Defining  $\beta$  relation between Weight ( $W$ ) as function of Energy (Total)

$$W = \frac{N!}{a_1! a_2! \dots a_n!}$$

$$W = \frac{N!}{\prod_j a_j!} \quad - (1)$$

The correlation between  $E$  and  $W$  is given by

$$\ln W = \ln \left( \frac{N!}{\prod_j a_j!} \right)$$

$$\ln(a_1 a_2) = \ln a_1 + \ln a_2$$

$$\therefore \ln W = \ln N! - \ln \prod_j a_j!$$

$$\therefore d \ln W = d (\ln N! - \ln \prod_j a_j!)$$

$$\therefore d \ln W = - \sum_n \ln a_n!$$

$$\therefore d \ln W = - \sum_n \ln a_n da_n \quad - (2)$$

(Stirling's Approximation)

$$\ln x! = x \ln x - x$$

$$\ln a_n! = a_n \ln a_n - a_n$$

$$\text{Probability of Occupying a given energy level} = P_n = \frac{a_n}{N} = \frac{e^{-\beta \epsilon_n}}{Z}$$

$$\therefore a_n = \frac{N e^{-\beta \epsilon_n}}{Z}$$

$$\frac{a_n}{a_0} = \frac{\frac{N e^{-\beta \epsilon_n}}{Z}}{\frac{N e^{-\beta \epsilon_0}}{Z}} = \frac{e^{-\beta \epsilon_n}}{e^{-\beta \epsilon_0}}$$

$$\text{But } \epsilon_0 = 0$$

$$\frac{a_n}{a_0} = e^{-\beta \epsilon_n} \quad \therefore a_n = a_0 e^{-\beta \epsilon_n}$$

$$\therefore \ln a_n = \ln a_0 + \ln(e^{-\beta \epsilon_n})$$

$$\therefore \ln a_n = \ln a_0 - \beta \epsilon_n \quad - (3)$$

$$\therefore d \ln W = - \sum_n (\ln a_0 - \beta \epsilon_n) da_n$$

$$= - \ln a_0 \sum_n da_n + \beta \sum_n \epsilon_n da_n$$

$$\sum_n \epsilon_n da_n = dE$$

$$\therefore d \ln W = \beta dE \quad \leftarrow$$

$N$  is constant.  
 $dN = 0$

$\beta$  must have units of inverse of energy

$$\beta = \frac{1}{kT}$$

k - Boltzmann Constant

T - Temperature (Absolute)

## Molecular Energy Levels

Monday, October 5, 2020 11:40 AM

The molecular partition function can be evaluated by considering molecular energy levels. For polyatomic molecules, there are four energetic degrees of freedom.

1. Translation
2. Rotation
3. Vibration
4. Electronic

Assuming that energetic degrees of freedom are not coupled.

So all these can be decomposed into a product of partition functions corresponding to each degree of freedom.

Let  $\epsilon_{\text{Total}}$  represents the energy associated with a given molecular energy level.

$$\epsilon_{\text{Total}} = \epsilon_T + \epsilon_R + \epsilon_V + \epsilon_E \quad \text{--- (1)}$$

Molecular partition function is given by

$$\begin{aligned} q_{\text{Total}} &= \sum g_{\text{Total}} e^{-\beta \epsilon_{\text{Total}}} \quad \text{--- (2)} \\ &= \sum (g_T g_R g_V g_E) e^{-\beta (\epsilon_T + \epsilon_R + \epsilon_V + \epsilon_E)} \\ &= \sum (g_T e^{-\beta \epsilon_T}) (g_R e^{-\beta \epsilon_R}) (g_V e^{-\beta \epsilon_V}) (g_E e^{-\beta \epsilon_E}) \end{aligned}$$

$$q_{\text{Total}} = q_T q_R q_V q_E \quad \text{--- (3)}$$

This relationship demonstrates that the total molecular partition function is simply the product of partition function for each molecular energetic degrees of freedom.

$$\therefore Q_{\text{Total}} = q_{\text{Total}}^N \quad (\text{distinguishable}) \quad \text{--- (4)}$$

$$Q_{\text{Total}} = \frac{1}{N!} q_{\text{Total}}^N \quad (\text{Indistinguishable}) \quad \text{--- (5)}$$

## Translational Partition Function :-

Monday, October 5, 2020 12:04 PM

For any Queries  
Suyash Agnihotri (M.Sc. Physics, CSIR NET  
Physics)  
Contact: 9167111308  
Email: agnihotrisuyash@gmail.com

A particle with mass 'm' is free to move in domain  $0 \leq x \leq a$ , where  $a$  is length of the box

$\therefore$  The partition function for translational Energy in one dimension becomes

$$q_{T, 1D} = \sum_{n=1}^{\infty} e^{-\frac{\beta n^2 h^2}{8ma^2}} \quad \text{--- (1)}$$

As numerous energy levels are accessible at room temperature

Therefore summation in equation (1) can be replaced by Integration.

$$q_T \approx \sum e^{-\beta \alpha n^2} \approx \int_0^{\infty} e^{-\beta \alpha n^2} dn$$

$$\alpha = \frac{h^2}{8ma^2}$$

$$\int_0^{\infty} e^{-\alpha x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{\alpha}}$$

$$\therefore q_T \approx \int_0^{\infty} e^{-\beta \alpha n^2} dn = \frac{1}{2} \sqrt{\frac{\pi}{\beta \alpha}} = \frac{1}{2} \left( \frac{\pi}{\beta \alpha} \right)^{1/2}$$

$\therefore$  Substituting value of  $\alpha$ , the translational function in one dimension becomes

$$q_{T, 1D} = \left( \frac{2\pi m}{h^2 \beta} \right)^{1/2} \cdot a$$

This expression can be simplified by defining the thermal de Broglie wavelength.

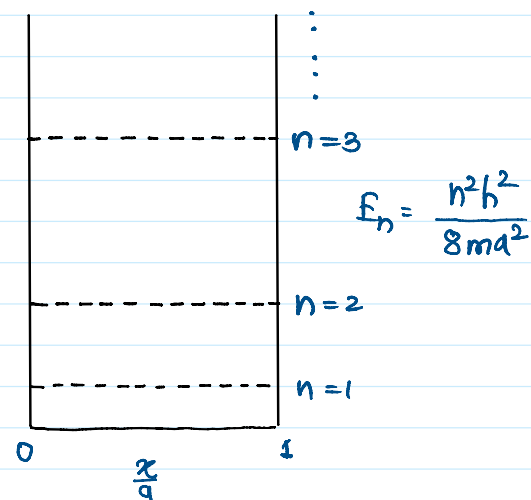
Thermal wavelength

$$\lambda = \left( \frac{h^2 \beta}{2\pi m} \right)^{1/2}$$

$$\therefore q_{T, 1D} = \frac{a}{\lambda} = \left( \frac{2\pi m}{\beta} \right)^{1/2} \cdot \frac{a}{h} = (2\pi m kT)^{1/2} \frac{a}{h} \quad \text{as } \beta = \frac{1}{kT}$$

$$\therefore q_{T, 1D} = (2\pi m kT)^{1/2} \frac{a}{h}$$

[Average momentum of gas particle  $P$  is equal to  $(mkT)^{1/2}$ ]



Particle in Box  
(Translational Energy levels)

[Average momentum of gas particle  $P$  is equal to  $(mkT)^{1/2}$ ]

$\therefore$  Translational partition function in 3 dimensions

$$\begin{aligned} q_{T,3D} &= q_{Tx} q_{Ty} q_{Tz} \\ &= \left(\frac{a_x}{\lambda}\right) \left(\frac{a_y}{\lambda}\right) \left(\frac{a_z}{\lambda}\right) \\ &= \left(\frac{1}{\lambda}\right)^3 a_x a_y a_z \\ &= \left(\frac{1}{\lambda}\right)^3 V \end{aligned}$$

$$\therefore q_{T,3D} = \frac{V}{\lambda^3} = (2\pi mkT)^{3/2} \cdot \frac{V}{h^3}$$

Where  $V$  is volume and  $\lambda$  is Thermal wavelength

$\therefore$  Translational partition function depends on both Volume & Temperature

## Equipartition Theorem:-

Monday, October 5, 2020 12:35 PM

Warning : These are Running Whiteboard Points not to be treated as only Reference for Exams

For any Queries

Suyash Agnihotri (M.Sc. Physics, CSIR NET Physics)

Contact: 9167111308

Email: agnihotrisuyash@gmail.com

The applicability of classical statistical mechanics to molecular system at high temperatures will be indicated in Equipartition Theorem.

The expression for the Three-dimensional partition function for molecule consisting of  $N$  atoms.

$$q_{\text{classical}} = \frac{1}{h^{3N}} \int \dots \int e^{-\beta H} dp^{3N} dx^{3N}$$

terms  $p$  and  $x$  represent the momentum and position coordinates for each particle respectively.

$H$  represents classical Hamiltonian like quantum Hamiltonian which is sum of kinetic and potential energy, therefore  $e^{-\beta H}$  is equivalent to  $e^{-\beta \epsilon}$  of quantum expression.

Consider the Hamiltonian for classical one dimensional harmonic oscillator. (with reduced mass  $\mu$ ) and force constant  $k$ .

$$H = \frac{p^2}{2\mu} + \frac{1}{2}kx^2$$

$$\therefore q_{\text{classical}} = \frac{1}{h} \int dp \int dx e^{-\beta \left( \frac{p^2}{2\mu} + \frac{1}{2}kx^2 \right)} = \frac{T}{\theta_v}$$

This result is in agreement with high temperature approximation to  $q_v$  using the quantum partition function.

**Statement:-**

The equipartition theorem states that any term in Classical Hamiltonian that is quadratic with respect to momentum or position will contribute  $\frac{kT}{2}$  to the average energy.

One dimensional Harmonic Oscillator  $\rightarrow$  'p' & 'x'

$\therefore$  Average energy by equipartition should be " $kT$ "

$\therefore$  For  $N$  Harmonic Oscillators  $= NkT$





Consider canonical ensemble and considering average energy of ensemble unit  $\langle E \rangle$ , which is simply total energy of ensemble by number of units in Ensemble. Let say  $(N)$

$$\therefore \langle E \rangle = \frac{E}{N} = \frac{\sum_n \epsilon_n a_n}{N} = \sum_n \epsilon_n \frac{a_n}{N} \quad - (1)$$

In this equation,  $\epsilon_n$  is the level energy and  $a_n$  is the occupation number of that energy level.

$\therefore$  The Boltzmann distribution for series of non-degenerate energy levels.

$$\frac{a_n}{N} = \frac{e^{-\beta \epsilon_n}}{q} \quad - (2)$$

Where 'q' is molecular partition function and  $\beta = (kT)^{-1}$  ( $q = e^{-\beta \epsilon_n}$ )

$$\therefore \langle E \rangle = \sum_n \epsilon_n \frac{a_n}{N} = \frac{1}{q} \sum_n \epsilon_n e^{-\beta \epsilon_n} \quad - (3)$$

Consider derivative of molecular partition function w.r.t.  $\beta$ .

$$\begin{aligned} \frac{dq}{d\beta} &= -\sum_n \epsilon_n e^{-\beta \epsilon_n} \\ \therefore -\frac{dq}{d\beta} &= \sum_n \epsilon_n e^{-\beta \epsilon_n} \quad - (4) \end{aligned}$$

$$\therefore \langle E \rangle = -\frac{1}{q} \left( \frac{dq}{d\beta} \right) = -\left( \frac{d \ln q}{d\beta} \right) \quad - (5) \quad \left( d \ln q = \frac{1}{q} dq \right)$$

$$\therefore E = N \langle E \rangle = -\frac{N}{q} \left( \frac{dq}{d\beta} \right) = -N \left( \frac{d \ln q}{d\beta} \right) \quad - (6)$$

Taking derivative of  $\beta$  w.r.t. time

$$\frac{d\beta}{dT} = \frac{d}{dT} (kT)^{-1} = -\frac{1}{kT^2} \quad - (7)$$

$$\therefore d\beta = \frac{-dT}{kT^2} \quad \therefore \frac{1}{d\beta} = \frac{-kT^2}{dT}$$

$$\therefore \langle E \rangle = kT^2 \left( \frac{d \ln q}{dT} \right) \quad - (8)$$

$$E = NkT^2 \left( \frac{d \ln q}{dT} \right) \quad - (9)$$

Total Energy E will change with temperature 'T'.

System approaches equilibrium by achieving the configuration of energy with maximum weight.

In other words the configuration of energy which will be observed at equilibrium corresponds to  $W_{\max}$ .

The tendency of system to maximize  $w$  and entropy  $S$  suggests that the relationship exists between these quantities. This relationship is given by

$$S = k \ln W$$

This relationship states that entropy is directly proportional to  $\ln(W)$  with Boltzmann constant serving as proportionality constant.

$\therefore$  Consider the energy of an ensemble of particles. This energy is equal to the sum of the product of the energies and the occupation numbers of these levels.

$$E = \sum_n \epsilon_n a_n \quad - (1)$$

$\therefore$  The total differential of  $E$  is given by

$$\therefore dE = \sum_n \epsilon_n da_n + \sum_n a_n d\epsilon_n \quad - (2)$$

2<sup>nd</sup> term of the equation becomes zero and change in Energy is related to changes in level occupation numbers only.

$$\therefore dE = \sum_n \epsilon_n da_n \quad - (3)$$

$\therefore$  The constraint of constant volume also dictates that there is no P-V type work.  
 $\therefore$  by the 1<sup>st</sup> law of thermodynamics the change in energy must be due to heat flow.

$$dE = dq_{\text{rev}} = \sum_n \epsilon_n da_n \quad - (4)$$

where  $dq_{\text{rev}}$  - is reversible heat exchange between system and surroundings the thermodynamic definition of entropy is.

$$dS = \frac{dq_{\text{rev}}}{T} \quad - (5)$$

$\therefore$  Comparing the last two equations give the following definition of entropy.

$$\therefore dS = \frac{1}{T} \sum_n \epsilon_n da_n \quad - (6)$$

Now

$$\beta = \frac{1}{kT} \quad \therefore \frac{1}{T} = \beta k$$

$$\therefore dS = k\beta \sum_n \epsilon_n da_n \quad - (7)$$

$$\therefore dS = k \sum_n \beta \epsilon_n da_n \quad - (8)$$

In Boltzmann distribution formula

$$\left( \frac{d \ln W}{d a_n} \right) + \alpha - \beta \epsilon_n = 0$$

$$\therefore \beta \epsilon_n = \left( \frac{d \ln W}{d a_n} \right) + \alpha \quad - (9)$$

Where  $\alpha$  and  $\beta$  are constants (Lagrangian Methods of Undetermined Multipliers)

$$\therefore dS = k \beta \sum_n \epsilon_n da_n = k \sum_n \left( \frac{d \ln W}{d a_n} \right) da_n + k \sum_n \alpha da_n$$

$$\therefore dS = k \sum_n \left( \frac{d \ln W}{d a_n} \right) da_n + k \alpha \sum_n da_n \quad (\text{zero})$$

$$\therefore dS = k \sum_n \left( \frac{d \ln W}{d a_n} \right) da_n$$

$$\therefore dS = k (d \ln W) \quad - (10)$$

$$\therefore S = k \ln W$$

This is the expression for Boltzmann formula for Entropy.

