Partition Function (Q)

INTRODUCTION:

The partition function is a dimensionless quantity. It summarizes in a convenient mathematical formas to how the energy of a system of molecule is partitional among the molecules. The partition function provides a bridge to link the microscopic properties of individual molecules such as their discrete energy levels moment of inertia with macroscopic properties like energy, heat capacity etc. of a system containing a large number of molecules. The importance of molecular partition function is that it contains all the information needed to calculate the thermodynamics properties of a system of independent particles.

**Ensemble:** A collection of large number of particle which is macroscopically same but microscopically different.

There are three types of ensembles.

Microcanonical ensemble : The ensemble in which all element have same macrostate represented by same number of particle N, same volume V and same energy E, i.e., macrostate is specified by (N, V, E) for all elements (systems). All elements of microcanonical ensemble are separated by impenetrable, rigid and non-interacting walls such that values of (N, V, E) for a particular system are not affected by the presence of other system, i.e., all systems are isolated to each other.

N, V, E	N, V, E	

- Walls of microcanonical ensembles are impenetrable, rigid, thermally non conducting.
- Used for adiabatic process.

Canonical ensemble : The ensemble in which all elements will have same macrostate represent by same N, V, T for all elements. The elements of a canonical ensemble are separated from each other by inpenetrable, rigid and conducting walls such that the values of N, V, T for a particular system are not affected by others. In canonical ensemble, each element is in thermal contact (equilibrium) with heat reservoir or with all other elements of the ensemble at temperature T. In this emsemble elements can exchange energy but not particles.

N, V, T

Impenetrable   Rigid   Thermally conducting
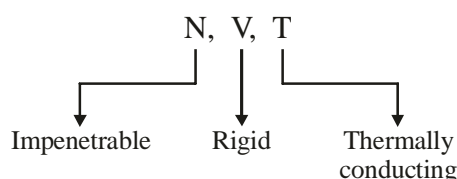
For isothermal

N, V, T	⇔	
⇕	⇔N, V, T	

Grand canonical ensemble : The ensemble in which all elements will have same macrostate represent by same μ, V, T for all elements. The elements of a grand canonical ensemble are separated from each other by penetrable, rigid and conducting walls such that the values of μ, V, T for a particular system aren't affected by others. In this ensemble the ensemble the elements are in contact with particle energy reservoir. The elements can exchange energy as well as particles.

$$\mu, \ V, \ T$$

Penetrable   Rigid   Thermally conducting
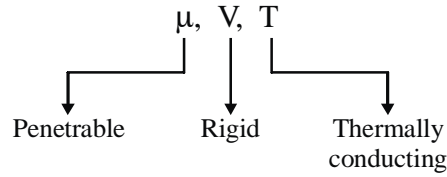
* It tells how the molecules are partitioned into given energy level.
* As wave function ψ has all the quantum information of the particles, the partition function has all the thermodynamic information.

$$q = \sum g_i \, e^{-\beta E_i} = \sum g_i \, e^{-E_i/kT}, \left[\beta = \frac{1}{kT} \right]$$

* The number of thermally accessible energy states is equal to partition function.

Note: In statistical thermodynamics all energies are calculated with respect to ground state. Energy of ground state is considered to be zero.

$$q = \sum g_i \, e^{-E_i/kT}$$

$$q = g_0 \, e^{-E_0/kT} + g_1 \, e^{-E_1/kT} + g_2 \, e^{-E_2/kT} + \cdots \quad (\because E_0 = 0)$$

$$q = g_0(1) + g_1 \, e^{-E_1/kT} + g_2 \, e^{-E_2/kT} \cdots$$

$$= g_0 + g_1 \, e^{-E_1/kT} + g_2 \, e^{-E_2/kT} \cdots$$

When $T \to 0$

$$= g_0 + g_1 \, e^{-E_1/k(0)} + g_2 \, e^{-E_2/k(0)} \cdots$$

$$q = g_0 + g_1(0) + g_2(0) + g_3(0) \cdots$$

$$\left[\begin{array}{l} e^{-0} = \dfrac{1}{e^0} = \dfrac{1}{1} = 1 \\[2mm] e^{-\infty} = \dfrac{1}{e^\infty} = \dfrac{1}{\infty} = 0 \\[2mm] e^{-E_1/k(0)} = e^{-E_1/0} = e^{-\infty} \end{array} \right.$$

$\boxed{\text{When } T \to 0, \ q = g_0}$

When $T \to \infty$

$$q = g_0 + g_1 \, e^{-E_1/k(\infty)} + g_2 \, e^{-E_2/k(\infty)}$$

$$\left[e^{-E/\infty} = e^{-0} = \dfrac{1}{e^0} = 1 \right.$$

$$q = g_0 + g_1 + g_2 + \cdots$$

$\boxed{q = \sum g_i}$

Since, T can never be 0 or ∞.

Therefore, molecule lie in between g_0 and g_∞.

$$\begin{array}{ll} \underline{\hspace{2cm}} & g_3 \\ \underline{\hspace{2cm}} & g_2 \\ \underline{\hspace{2cm}} & g_1 \end{array} \Big] \text{When } T = \infty$$

$$g = 0 \ \underline{\hspace{3cm}} \text{When } T = 0$$

Problem: The relative population of the state of a two level system when $T \to \infty$ is

Soln. $\dfrac{n_j}{n_i} = \dfrac{g_j}{g_i} \, e^{-\Delta E/kT} = \dfrac{1}{1} e^{-\Delta E/kT} = e^{-\Delta E/k\infty} = e^{-0} = \dfrac{1}{e^0} = 1$

Problem: A system of N particles has among other two energy levels with $g_1 = 2$, $g_2 = 3$, $U_1 = 41.84$ kJ/mol and $U_2 = 58.58$ kJ/mol. Calculate the ratio of number of particles in two energy states at 1000 K.

Soln.

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} e^{-\Delta E/kT}$$

$$\Delta E = U_2 - U_1 = 58.58 \text{ kJ/mol}$$

$$= 16.74 \text{ kJ/mol}$$

For 1 mole : $\Delta E = 16.74$ kJ

6.023×10^{23} molecule $\Delta E = 16.74$ kJ

For 1 molecule $= \dfrac{16.74}{6.023 \times 10^{23}}$ kJ

$$\therefore \quad \frac{n_2}{n_1} = \frac{3}{2} \exp\left(-\frac{16.74 \times 10^3 \text{ J}}{\dfrac{6.023 \times 10^{23}}{1.38 \times 10^{-23}} \dfrac{\text{J}}{\text{K}} \times 1000 \text{ K}}\right) \Rightarrow \frac{n_2}{n_1} = 0.201$$

TRANSLATIONAL PARTITION FUNCTION

$$q_t = \sum g_t e^{-\beta E_{trans}} = \sum g_t e^{-\frac{E_{trans}}{kT}}$$

From quantum mechanics $E_{trans.} = \dfrac{n^2 h^2}{8m \ell_x^2}$ $g_t = 1$

$$q_t = \sum_{n=1}^{\infty} 1 \cdot e^{-\frac{n^2 h^2}{8m\ell^2 kT}} = \int_1^{\infty} e^{-\frac{n^2 h^2}{8m\ell^2 kT}} dn \text{ (Summation is discrete and integration is continuous)}$$

$$= \int_0^{\infty} e^{-\frac{n^2 h^2}{8m\ell^2 kT}} dn = \int_0^{\infty} n^0 e^{-\alpha n^2} dn = \frac{\left|\underline{0+1/2}\right.}{2\alpha^{0+1/2}} = \frac{\sqrt{\pi}}{2\sqrt{\alpha}} = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} = \frac{1}{2}\sqrt{\frac{8m\ell^2 kT\pi}{h^2}}$$

$$= \frac{1}{2}\sqrt{\frac{8mkT\pi}{1}} \times \frac{\ell_x}{h} = \sqrt{2mkT\pi}\,\frac{\ell_x}{h}$$

$$q_{t_x} = \frac{\dfrac{\ell_x}{h}}{\dfrac{1}{\sqrt{2mkT\pi}}} \to \Lambda = \text{de-Broglie wavelength}$$

$$q_{t_y} = \frac{\ell_y}{\Lambda} \text{ and } q_{t_z} = \frac{\ell_z}{\Lambda}$$

$$(q_T)_{trans.} = q_{t_x} \cdot q_{t-y} \cdot q_{t-z} = \frac{\ell_x}{\Lambda} \cdot \frac{\ell_y}{\Lambda} \cdot \frac{\ell_z}{\Lambda} = \frac{\ell_x \cdot \ell_y \cdot \ell_z}{\Lambda^3}$$

$$\boxed{q_t = \frac{V}{\Lambda^3}}, \text{ where } \Lambda = \frac{h}{\sqrt{2mkT\pi}}$$

Problem-1: The translational partition function has the unit of

(a) V   (b) 1/V   (c) P   (d) a number

Soln. We know the partition function is just the normalization factor in calculating the probability and hence it is a dimensionless number hence it's unit is a number

Correct option is (d)

Problem-2: For an ideal monatomic gas, the particle partition function 'q' is

(a) $\left(\dfrac{8\pi mkT}{h^2}\right)^{3/2} V$ (b) $\left(\dfrac{2\pi mkT}{h^2}\right)^{3/2} V$ (c) $\left(\dfrac{h^2}{8\pi mkT}\right)^{3/2} V$ (d) $\left(\dfrac{h^2}{2\pi mkT}\right)^{3/2} V$

Soln. For an ideal monatomic gas, only translational degrees of freedoms are there. Hence the partition function is given by

$$q_t = \frac{V}{\lambda^3} \text{ where } \lambda = \frac{h}{\sqrt{2\pi mkT}}$$

$$q = \frac{V}{h^3} \times \left(2\pi mkT\right)^{3/2}$$

$$q = \left(\frac{2\pi mkT}{h^3}\right)^{3/2} V$$

Correct opion is (b)

Problem: The translational partition function (q) for the H_2 molecule in a 100 cm^3 vessel at 298 K is 2.77×10^{26}. The q for the D_2 molecule under the same condition would be

(a) 5.54×10^{26} (b) 3.29×10^{26}

(c) 21.25×10^{26} (d) 7.83×10^{26}

Soln. Translational partition function in 3-dimension is given by

$$q_t = \frac{V}{\lambda^3}, \text{ Where } V = \text{volume of system}$$

$$\lambda = \frac{h}{\sqrt{2\pi mkT}} \Rightarrow \boxed{q_t \alpha\, m^{3/2}} \Rightarrow \frac{(q_t)_{D_2}}{(q_t)_{H_2}} = \left(\frac{m_{D_2}}{m_{1+2}}\right)^{3/2}$$

$$(q_t)_{D_2} = (q_t)_{H_2} \cdot (2)^{3/2} = 2.77 \times 10^{26} \times (2)^{3/2}$$

$$(q_t)_{D_2} = 7.83 \times 10^{26}$$

Correct option is (d)

(a) Internal energy (U_{trans}):

$$U_{trans.} = NkT^2 \left(\frac{\partial \ln q_t}{\partial T}\right)_V$$

$$q_t = \frac{V}{\left(\dfrac{h}{\sqrt{2m\pi kT}}\right)^3} \Rightarrow q_t \propto T^{3/2} \Rightarrow \ln q_t \propto \ln T^{3/2}$$

$$\left(\frac{\partial \ln q_t}{\partial T}\right)_V = \frac{3}{2}\frac{\partial}{\partial T}\ln T = \frac{3}{2T}$$

$$\therefore \quad U_{trans.} = NkT^2\left(\frac{3}{2T}\right) = \frac{3}{2}NkT$$

For 1 mole $U_{trans.} = \frac{3}{2}N_A kT \Rightarrow \boxed{U_{trans.} = \frac{3}{2}RT}$

(b) Pressure:

$$P = NkT\left(\frac{\partial \ln q_t}{\partial V}\right)_T$$

Now, $q_t = \frac{V}{\Lambda^3} \Rightarrow q_t \propto V \Rightarrow q_t \propto V \Rightarrow \ln q_t \propto \ln V$

$$\left(\frac{\partial \ln q_t}{\partial V}\right)_T = \frac{1}{V}$$

$$\therefore \quad P = NkT\left(\frac{1}{V}\right) \Rightarrow PV = NkT$$

For 1 mole $PV = N_A kT \Rightarrow PV = RT$

(c) Enthalpy (H):

$H = U + PV$

For 1 molar, $H_m = U_m + PV = \frac{3}{2}RT + RT \Rightarrow H_m = \frac{5}{2}RT$

(d) $(C_P)_m = \left(\frac{\partial H}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\frac{5}{2}RT\right]_P = \frac{5}{2}R$

$$(C_V)_m = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T}\left[\frac{3}{2}RT\right]_V = \frac{3}{2}R$$

$$\frac{C_P}{C_V} = \gamma = 1 + \frac{2}{f} = 1 + \frac{2}{3} = \frac{5}{3}; \; f = \text{degree of freedom}$$

(e) Entropy:

Sackur-Tetrode equation:

$$S_{trans.} = Nk\ln\frac{q_t}{N} + \frac{U}{T} + Nk$$

$$= Nk\ln\frac{V}{\Lambda^3 N} + \frac{U}{T} + Nk$$

$$= Nk\ln\frac{V}{\Lambda^3 N} + \frac{3}{2}\frac{NkT}{T} + Nk$$

$$= Nk\ln\frac{kT}{P\Lambda^3} + \frac{5}{2}Nk$$

$$= Nk\left[\ln\frac{kT}{P\Lambda^3} + \frac{5}{2}\right] = Nk\left[\ln\frac{kT}{P\Lambda^3} + \ln e^{5/2}\right]$$

$$S_{\text{trans.}} = Nk \ln \frac{kT}{P\Lambda^3} e^{5/2} \qquad \left[\log_e e^{5/2} = \frac{5}{2} \log_e e = \frac{5}{2} \right]$$

$S_{\text{trans.}}$ depends on Λ. $\qquad \left[V = \frac{NkT}{P} \right]$

$$S = Nk \ln \frac{q_t}{N} + \frac{U_t}{T} + Nk$$

$$= Nk \ln \frac{V}{\left[\dfrac{h}{\sqrt{2\pi mkT}} \right]^3 N} + \frac{3}{2} Nk + Nk$$

$$= Nk \ln \frac{NkT}{P \dfrac{h^3 \cdot N}{(2\pi mkT)^{3/2}}} + \frac{5}{2} Nk$$

$$S = Nk \ln \frac{k^{5/2}}{h^3} \left[\frac{(2\pi)^{3/2} T^{5/2} Au^{3/2} \cdot M^{3/2}}{P} \right] + \frac{5}{2} Nk$$

$$S_m = N_A k \ln \frac{k^{5/2} (2\pi)^{3/2} Au^{3/2}}{h^3} \left(\frac{T^{5/2} M^{3/2}}{P} \right) + \frac{5}{2} N_A k$$

$$S_m = R \ln \frac{k^{5/2} (2\pi)^{3/2} Au^{3/2}}{h^3} \left(\frac{T^{5/2} M^{3/2}}{P} \right) + \frac{5}{2} R$$

$$S_m = R \left[-1.1514 + \frac{5}{2} \ln T + \frac{3}{2} \ln M - \ln \frac{P}{P_0} \right]$$

$$S_{\text{trans.}} = Nk \ln \frac{kT}{P\Lambda^3} e^{5/2}$$

Problem: Evaluate $q_{\text{trans.}}$ for O atom at 300 K contained in a volume of 22.414 dm^3.

Soln. $q_{\text{trans.}} = \dfrac{V}{\Lambda^3}$; $V = 22.414$ dm^3, $T = 300$ K

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}} = \frac{6.626 \times 10^{-34}\ \text{J s}}{\sqrt{2 \times 3.14 \times 16 \times 1.38 \times 10^{-23}\ \frac{\text{J}}{\text{K}} \times 300\,\text{K} \times 1.66 \times 10^{-27}\ \text{kg}}}$$

$$= \frac{6.626 \times 10^{-34}}{69053.87 \times 10^{-25}} = 0.025 \times 10^{-9} = 2.52 \times 10^{-11}\ \text{m}$$

$$q = \frac{22.414\ \text{dm}^3}{(2.52 \times 10^{-11}\ \text{m})^3} = \frac{22.414 (10^{-1}\ \text{m})^3}{(2.52 \times 10^{-11})^3\ \text{m}^3} = 1.40 \times 10^{30}$$

Problem: Calculate the translational contribution to:

S_m U_m A_m G_m for He at 25 °C

Soln. $U_m^0 = \dfrac{3}{2}RT = \dfrac{3}{2} \times 8.314 \dfrac{J}{mol\text{-}K} \times 298\,K = 3716.4 \dfrac{J}{mol}$

$H_m^0 = \dfrac{5}{2}RT = \dfrac{5}{2} \times 8.314 \dfrac{J}{mol\text{-}K} \times 298\,K = 6193.9 \dfrac{J}{mol}$

$S_m^0 = R \left[-1.1514 + \dfrac{5}{2}\ln T + \dfrac{3}{2}\ln M - \ln\dfrac{P}{P_0} \right]$

$\qquad = R \left[-1.1514 + \dfrac{5}{2}\ln 298 + \dfrac{3}{2}\ln 4 - \ln\dfrac{P_0}{P_0} \right] = 8.314\dfrac{J}{mol\text{-}K}\left[-1.1514 + \dfrac{5}{2}\ln 298 + \dfrac{3}{2}\ln 4 \right]$

$\qquad = 126.1 \dfrac{J}{mol\text{-}K}$

$A_m^0 = U_m^0 - TS_m^0 = 3716.4 - 298 \times 126.1 = -33861.4 \dfrac{J}{mol}$

$G_m^0 = H_m^0 - TS_m^0 = -31382.9 \dfrac{J}{mol\text{-}K}$

ROTATIONAL PARTITION FUNCTION

$q_{rot.} = \sum g_{rot.}\, e^{-E_{rot.}/kT}$

$g_{rot.} = 2J+1$

$E_{rot.} = \underset{\underset{in\ joule}{\downarrow}}{B}\ J(J+1)$; $q_{rot.} = \displaystyle\sum_{J=0}^{\infty} (2J+1)e^{-\frac{BJ(J+1)}{kT}}$

Under high temperature approx.: At high temperature summation changed into integration, because system becomes continuous, because molecules present in higher energy level.

$q_{rot.} = \displaystyle\int_0^{\infty} (2J+1)\, e^{-\frac{BJ(J+1)}{kT}}\, dJ = \int_0^{\infty} (2J+1)e^{-\alpha(J^2+J)}\, dJ$

$\qquad = \displaystyle\int_0^{\infty} e^{-\alpha(J^2+J)}(2J+1)\, dJ$

$\qquad = \displaystyle\int_0^{\infty} e^{-\alpha t}\, dt = \left[\dfrac{e^{-\alpha t}}{-\alpha} \right]_0^{\infty}$ $\qquad \left[\begin{array}{l} J^2 + J = t \\ 2J+1 = dt/dJ \\ (2J+1)\,dJ = dt \end{array} \right.$

$\qquad = \dfrac{-1}{-\alpha}\left[e^{-\alpha \times \infty} - e^{-\alpha(0)} \right]$

$\qquad = -\dfrac{1}{\alpha}\left[e^{-\infty} - e^{-0} \right] = -\dfrac{1}{\alpha}[0-1] = \dfrac{1}{\alpha}$

If B is in Joule. Therefore, $q_{rot.} = \dfrac{1}{\alpha} = \dfrac{kT}{B} = \dfrac{\frac{J}{K} \times h}{J}$

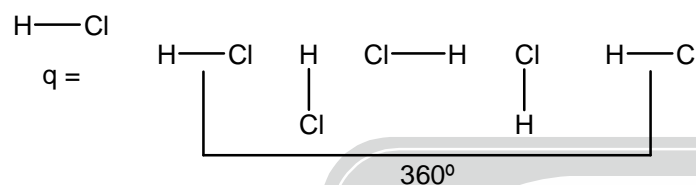If B is in cm^{-1} $q_{rot.} = \dfrac{kT}{\underbrace{B\,hc}_{J}}$ $B = cm^{-1}$

Therefore, $q_{rot.} = \dfrac{T}{B\,hc/k} \Rightarrow \theta_r =$ characteristic rotation temp.

As q has no unit.

$q_{rot.} = \dfrac{T}{\theta_r}$ $\left[\text{Valid only when } \dfrac{T}{\theta_r} \geq 100\right]$

$\theta_r = \dfrac{B\,hc}{k}$ and $B = \dfrac{h}{8\pi^2\,Ic}$; $\theta_r = \dfrac{hhc}{\dfrac{8\pi^2 Ic}{k}} \Rightarrow \theta_r = \dfrac{h^2}{8\pi^2 Ik}$

q =   H——Cl | H——Cl | H   Cl——H   Cl   H——C
                         Cl   H
                    $\underbrace{\hspace{5cm}}_{360^\circ}$

q =   H——H | H——H | H   H——H   H   H——H
                        H   H
                   $\underbrace{\hspace{5cm}}_{360^\circ}$
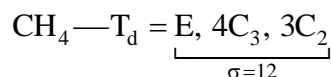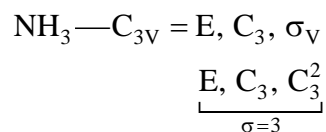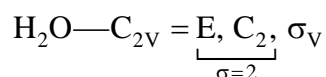
H——H two times comes.

$q = \dfrac{T}{2\theta_r}$ for H_2

Symmtry number (σ): Number of indistinguishable configuration which a molecule acquires during a rotation of 360° due to these indistinguishable configuration formula of rotational partition function gets modified to

$$\boxed{q_{rot.} = \dfrac{T}{\sigma\theta_r} = \dfrac{kT}{\sigma B\,hc}}$$

For example:

HCl	$\sigma = 1$	H_2O	$\sigma = 2$
H—H	$\sigma = 2$	Benzene	$\sigma = 12$
NH_3	$\sigma = 3$	Pyridine	$\sigma = 2$
CH_4	$\sigma = 12$		

H_2O—$C_{2V} = \underbrace{E, C_2, \sigma_V}_{\sigma = 2}$

NH_3—$C_{3V} = E, C_3, \sigma_V$

$\underbrace{E, C_3, C_3^2}_{\sigma = 3}$

CH_4—$T_d = \underbrace{E, 4C_3, 3C_2}_{\sigma = 12}$

Problem: The rotational partition function (q^R) of an AB molecule at 27°C is 19.6. What would be its q^R at 327°C?

(a) 19.6   (b) 27.7   (c) 39.2   (d) 55.3

Soln. For A–B molecule rotational partition function is given by

$q^R = \dfrac{T}{\theta_r}$ where θ_r = chracterstic rotation temperature

$$\boxed{q^R \alpha\, T}$$

$\dfrac{q^R(327°C)}{q^R(27°C)} = \dfrac{(273+327)\text{kelvin}}{(273+27)\text{kelvin}}$

$q^R(327°C) = \dfrac{600}{300} \times q^R(27°C)$

$q^R(327°C) = 2 \times 19.6 = 39.2$

Correct option is (c)

Internal energy:

$U = NkT^2 \left(\dfrac{\partial \ln q}{\partial T}\right)_V$

$q = \dfrac{T}{\sigma\theta_r} \Rightarrow q \propto T \Rightarrow \ln q \propto \ln T$

$\left(\dfrac{\partial \ln q}{\partial T}\right)_V = \dfrac{1}{T}$

$\therefore\ \ U = \dfrac{NkT^2}{T} = NkT$

$\therefore\ \ U_m^0 = N_A kT = RT$

Enthalpy:

$H_m^0 = U_m^0 = RT$ (As in rotation no change in volume, $\therefore\ H = U$)

Entropy:

$S = Nk \ln q + \dfrac{U}{T} = Nk \ln \dfrac{T}{\sigma\theta_r} + \dfrac{NkT}{T}$

$S = Nk \left\{\ln \dfrac{T}{\sigma\theta_r} + 1\right\}$ $G = A = -NkT \ln q$

$G_m^0 = A_m^0 = -RT \ln q_{rot.}$

For linear rotor : $q = \dfrac{kT}{\sigma\, B\, hc} = \dfrac{T}{\sigma\theta_r}$

For asymmetric molecules : $q = \dfrac{1}{\sigma} \left(\dfrac{kT}{hc} \right)^{3/2} \left(\dfrac{\pi}{ABC} \right)^{1/2}$

where A, B and C are rotational constants along the different axes of rotations.

$$q(T) = \underbrace{\left(\dfrac{k_B T}{hc} \right)^{3/2}}_{\text{Rotational}} \underbrace{\left(\dfrac{8\pi^3 m k_B T}{h^2} \right)^{3/2}}_{\text{Translation}}$$

$$U = \dfrac{3}{2} RT + \dfrac{3}{2} RT ; \quad C_V = \dfrac{3}{2} R + \dfrac{3}{2} R = 3R$$

Problem: (a) Calculate characteristic rotational temperature for N_2 molecule given temperature distance = 109.76 pm.

Soln. $\theta_r = \dfrac{h^2}{8\pi^2 I k}$ and $I = \mu r^2 \Rightarrow \mu_{N_2} = \dfrac{m_N \cdot m_N}{m_N + m_N}$

$\qquad = \dfrac{14}{2} = 7 \text{ g/mol} = 7 \times 1.67 \times 10^{-27} \text{ kg}$

$\theta_r = \dfrac{(6.626 \times 10^{-34} \text{ J s})^2}{8 \times (3.14)^2 \times 7 \times 1.66 \times 10^{-27} \times 109.76 \times 10^{-12} \times 1.38 \times 10^{-23} \frac{J}{K}}$

$\qquad = \dfrac{(6.626)^2 \times (10^{-34})^2 (\text{J s})^2}{8 \times (3.14)^2 \times 1.40 \times 10^{-46} \text{ kg m}^2 \times 1.38 \times 10^{-12} \frac{J}{K}}$

$\qquad = 2.88 \dfrac{\text{J s}^2 \text{ K}}{\text{kg m}^2} = 2.88 \text{ K} \qquad 1 \text{ J} = \text{kg m}^2 \text{ s}^2$

Problem: (b) Find out the rotational partition function at 500 K

Soln. $q = \dfrac{T}{\sigma \theta_r} = \dfrac{500 \text{ K}}{2 \times 2.88 \text{ K}} = \dfrac{500}{5.76} = 86.80$

Problem: Calculate rotational contribution to interval energy, enthalpy and Gibbs free energy for O_2 molecule at 500 K. Given internuclear distance of $O_2 = 121 \text{ pm}$.

Soln. $U_m^0 = RT = H_m^0 = 8.314 \dfrac{J}{\text{mol-K}} \times 500 \text{ K} = 4157 \dfrac{J}{\text{mol}}$

$\qquad G = -RT \ln q = -RT \ln \dfrac{T}{\sigma \theta_r}$

Now, $\theta_r = \dfrac{h^2}{8\pi^2 I k} = \dfrac{h^2}{8\pi^2 \mu r^2 k} \left\{ \mu = 1.66 \times 10^{-27} \times \dfrac{m_0}{2} \right\}$

$\qquad = \dfrac{(6.626 \times 10^{-34} \text{ J-s})^2}{8 \times (3.14)^2 \times 1.66 \times 10^{-27} \times \dfrac{16}{2} \text{ kg} \times (121 \times 10^{-12} \text{ m})^2 \times 1.38 \times 10^{-23} \dfrac{J}{K}}$

$\qquad = 2.07 \text{ K}$

$$q = \frac{T}{\sigma\,\theta_r} = \frac{500\,K}{2 \times 2.07\,K} = 120.77$$

$$G = -RT\ln q$$

$$= -RT\ln\frac{T}{\sigma\,\theta_r}$$

$$= -8.314\,\frac{J}{mol\text{-}K} \times 500\,K\,\ln(120.77)$$

$$= -19928.7\,J/mol$$

$$A = -19928.7\,J/mol$$