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"Unimolecular Reaction Dynamics *from Lindemann-Hinshelwood Theory to RRKM Theory*"

Started Mar.01.2019, Last modified Mar.27.2020

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1. Prelude to unimolecular reaction

We learned three major gas phase reaction mechanisms during freshman chemistry as below

$$\text{Reactant} \rightarrow \text{Product(s)} \tag{1}$$

$$\text{Reactant 1} + \text{Reactant 2} \rightarrow \text{Product(s)} \tag{2}$$

$$\text{Reactant 1} + \text{Reactant 2} + \text{M} \rightarrow \text{Product(s)} + \text{M} \tag{3}$$

(where M is the third-body molecule)

From (1) to (3), each mechanism is called *unimolecular reaction*, *bimolecular reaction*, *termomolecular reaction.* Surely, as you can see, unimolecular reaction seems to be the simplest reaction. However, Fermat's Last Theorem looks simple on the surface at least and it had tortured many great beautiful minds for over almost 400 years before it was finally proved by Sir Andrew Wiles in 1995. In case of this simply look reaction, it turned out to be surprisingly complicated and difficult to make good agreement between theoretical explanations and experimental data. Here, we will mainly focus on the timeline of the development of the theories starting from Lindemann-Hinshelwood theory to RRKM theory. Historical background will come first followed by deeper explanations. I mainly followed the stream based on **Chemical Kinetics and Dynamics 2nd edition** written by Jeffrey I. Steinfeld, Joseph S. Francisco and Wiliam L. Hase. So if you want to study deeper, I recommend you to revisit this book.

2. Lindemann-Hinshelwood Theory: collisional-activation mechanism

In 1922, Lindemann proposed a collisional-activation mechanism theory for thermal unimolecular reactions. In his paper, he mentioned that unimolecular reaction happens as below

$$\text{A} + \text{M}^* \xrightarrow{k_1} \text{A}^* + \text{M} \tag{4}$$

$$\text{A}^* + \text{M} \xrightarrow{k_{-1}} \text{A} + \text{M}^* \tag{5}$$

$$\text{A}^* \xrightarrow{k_2} \text{Product(s)} \tag{6}$$

Here, A represents the reactant and M is the third-body molecule that collide with A. A^* represents a molecule with sufficient energy to react and M^* is the third-body molecule with energy, which could be A itself. (4) describes bimolecular collisions in which energy in M being transferred to A by collision with rate coefficient k_1. Energized A^* can go through deactivation by collision with M again as described in (5) or decomposition to the products as described in (6). It is assumed that reaction (5) is so efficient that every collision event between A^* and M will end up being A and M^* one hundred percent. This assumption is so-called '*strong collision assumption*' for de-energizing reactant. This means that rate coefficient k_{-1} is equal to the gas-kinetic collision number Z_1 which is already calculated in gas-kinetic theory.

Okay, if we apply the steady-state hypothesis with regard to the concentration of A^*, the overall rate of unimolecular reaction with regard to [A] would become as below

$$\text{unimolecular reaction rate} = k_{uni}[A] = k_2[A^*]$$

and due to steady-stead assumption,

$$\frac{d[A^*]}{dt} = 0 = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M]+k_2} \tag{7}$$

If we apply (7) to $k_2[A^*]$,

$$\text{unimolecular reaction rate} = k_{uni}[A] = \frac{k_1k_2[A][M]}{k_{-1}[M] + k_2}$$

As a result,

$$k_{uni} = \frac{k_1k_2[M]}{k_{-1}[M]+k_2} \tag{8}$$

This equation (8) have two major expressions for k_{uni} under different conditions.

First, at high pressure condition where [M] $\rightarrow\infty$, we can ignore k_2 in the denominator in (8).

$$k_{uni,\infty} = \frac{k_1k_2}{k_{-1}} \sim \frac{[A^*]}{[A]} \times k_2 \tag{9}$$

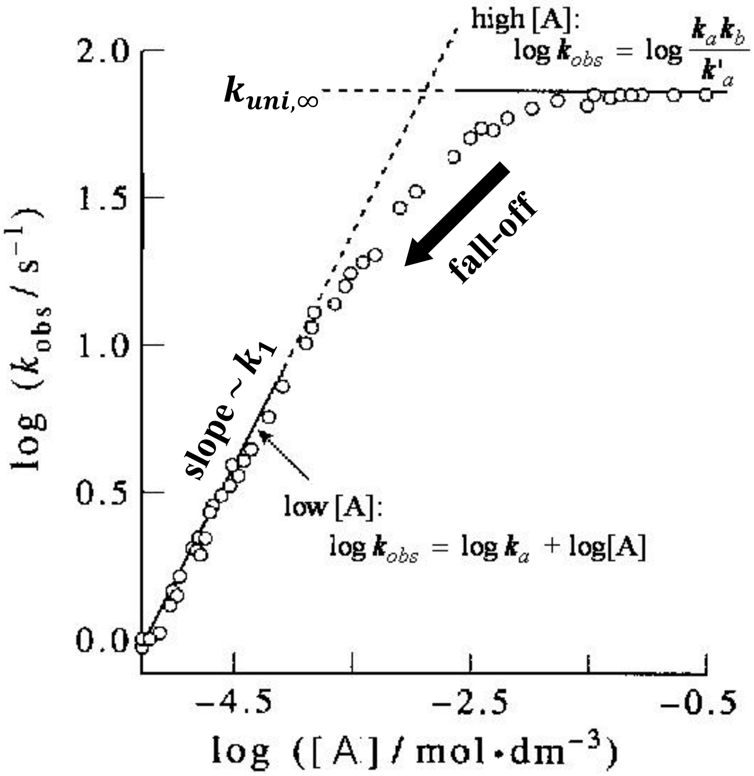
As you can see above, $\frac{[A^*]}{[A]}$ represents the probability that the molecule is energized by collision and this represents the unimolecular reaction rate constant at high pressure.

Second, at low pressure condition where [M] $\rightarrow 0$, we can ignore $k_{-1}[M]$ in the denominator in (8).

$$k_{uni,0} = k_1[M] \tag{10}$$

It is clear that (9) would result in first order reaction mechanism when combined with [A] and (10) would result in second order reaction mechanism when combined with [A].

So Lindemann beautifully and qualitatively explained that at lower pressure, the unimolecular reaction rate constant would linearly increase and then at higher pressure, this will converge to constant value as described in below figure.



([A] described in the figure above actually represents [M] in this paper. k_a is equal to k_1, k'_a corresponds to k_{-1} and k_b corresponds to k_2. Open circles are experimentally observed values.)

And the transition from the high-pressure rate constant $k_{uni,\infty}$ to $k_{uni,0}$ is called *Lindemann fall-off region*. Usually, chemists denotes $P_{1/2}$ as the pressure at which $\frac{k_{uni}}{k_{uni,\infty}} = \frac{1}{2}$ and you can get as below

$$P_{1/2} = \frac{k_{uni,\infty}}{k_1} \tag{11}$$

By modifying (8) with (9) and (10), we can get the expression for unimolecular reaction as below.

$$k_{uni} = \frac{k_{uni,\infty}}{1+\frac{k_{uni,\infty}}{k_{uni,0}}} = \frac{k_{uni,\infty}}{1+\frac{k_{uni,\infty}}{k_1[M]}} \tag{12}$$

It is relatively easy to find $k_{uni,\infty}$ from experiment. So, the first try would be matching the experimental value of k_1 with theoretical prediction. k_1 was first calculated from the line-of-centers collision theory expression as below.

$$k_1 = Z_1 \exp\left(-\frac{E_0}{k_B T}\right) \tag{13}$$

Where E_0 is simply equated to the high-pressure activation energy E_∞. However, this calculation turned out to show significant discrepancy from the experiment: The theory predicts fall-off region showing up at much higher pressure as compared to the experiment. Since the line-of-centers energization rate constant equation (13) only considers the frequency of collisions whose relative kinetic energy along the line of centers is greater than or equal to E_0, there is no information about the internal energy of the reactant molecule. In 1926, Hinshelwood added the contribution of the internal degrees of freedom and classical probability of internal energy in the range from E to $E + dE$ to the relative motion in order to overcome the threshold energy E_0. Since larger the molecule is (having larger number of internal degrees of freedom), higher becomes the probability that a molecule can store huge energy greater than E_0. As a result, energization rate constant $k_1$is larger for a complex reactant molecule than for a simple one. Assuming classical degrees of freedom s for a certain reactant molecule, Hinshelwood found that dk_1 is energy dependent and after long derivation, it can be described as below.

$$k_1 = \frac{Z_1}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} \exp\left(-\frac{E_0}{k_B T}\right) \tag{14}$$

The above equation can be interpreted that the energization rate constant is a product of two terms: the line-of-centers hard sphere collision rate constant Z_1 and the probability that the total energy of s classical harmonic oscillators for the reactant molecule exceeds E_0, which can be derived from classical statistical mechanics (Derivation can be found in A2-33 in Appendix 2 of **Chemical Kinetics and Dynamics 2nd edition** written by Jeffrey I. Steinfeld, Joseph S. Francisco and Wiliam L. Hase).
Now, if we apply (14) into (9), we can get

$$k_{uni,\infty} = \frac{Z_1 k_2}{k_{-1}(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} \exp\left(-\frac{E_0}{k_B T}\right)$$

Here, note that we are assuming strong collision assumption. For this reason, we can say $Z_1 = k_{-1}$ and as a result,

$$k_{uni,\infty} = \frac{k_2}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} \exp\left(-\frac{E_0}{k_B T}\right) \tag{15}$$

These (14) and (15) form the basis of ***Lindemann-Hinshelwood Theory*** of thermal unimolecular reactions. Lindemann fall-off curves calculated with this theory show significant improvement as compared to those calculated by Lindemann theory. However, significant discrepancies are still found between theoretical and experimental k_{uni} curves versus [M] at low pressure region.
Recall (9)

$$k_{uni,\infty} = \frac{k_1 k_2}{k_{-1}}$$

Since $k_{uni,\infty}$ and k_{-1} are constant in the assumption, if k_1 increases with s in Lindemann-Hinshelwood theory, the dissociation rate constant k_2 should decrease with s. Thus, the lifetime $\tau = {}^{1}/_{k_2}$ of the energized molecule (A^*) increases when the molecule has a greater number of degrees of freedom s. This is somewhat intuitively expected since when the molecule can store energy more efficiently with more degrees of freedom, energized molecule can stay more stabilized, thus resulting in prolonged lifetime. However, at the same time, it is also reasonable to think about the energy dependency of k_2. Higher the energy, there would be better chance for the molecules to decompose by increased k_2. Since Lindemann-Hinshelwood theory assumes that k_2 is energy independent constant, there had been several works to consider the energy dependent k_2.

3. k_2 as energy dependent rate constant *k(E)*

Let us refresh!!

$$\mathrm{A} + \mathrm{M}^* \xrightarrow{dk_1} \mathrm{A}^*(E, E + dE) + \mathrm{M} \tag{16}$$

$$\mathrm{A}^*(E, E + dE) + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}^* \tag{17}$$

$$\mathrm{A}^*(E, E + dE) \xrightarrow{k_2} \mathrm{Product(s)} \tag{18}$$

So, in (16), Hinshelwood considered the energy dependency of dk_1 and formulated k_1. Strong collision assumption has been made in (17), which is energy independent. Now, in this section, we will discuss how statistical theories have been used to calculate k_2 as a function of energy, expressed as *k(E)*. If we apply the steady-state approximation to the energized intermediate $\mathrm{A}^*(E, E + dE)$, we can get as below,

$$\frac{d\mathrm{A}^*(E, E + dE)}{dt} = 0 = dk_1[A][M] - k_{-1}\mathrm{A}^*(E, E + dE)[M] - k(E)\mathrm{A}^*(E, E + dE)$$

$$\mathrm{A}^*(E, E + dE) = \frac{dk_1[A][M]}{k_{-1}[M] + k(E)}$$

$$dk_{uni}(E, E + dE)[A] = k(E)\mathrm{A}^*(E, E + dE) = \frac{k(E)dk_1[A][M]}{k_{-1}[M] + k(E)}$$

$$dk_{uni}(E, E + dE) = \frac{k(E) \times {}^{dk_1}\!/_{k_{-1}}}{1 + {}^{k(E)}\!/_{k_{-1}[M]}}$$

$$k_{uni} = \int_{E_0}^{\infty} \frac{k(E) \times {}^{dk_1}\!/_{k_{-1}}}{1 + {}^{k(E)}\!/_{k_{-1}[M]}} = \omega \int_{E_0}^{\infty} \frac{k(E) \times {}^{dk_1}\!/_{k_{-1}}}{\omega + k(E)}$$

$$(\because k_{-1}[M] = \omega; \text{collision frequency})$$

And as we discussed in equation (9),

$\frac{k_1}{k_{-1}} = \frac{[A^*]}{[A]}$ represents the probability that the molecule is energized by collision and this represents the unimolecular reaction rate constant at high pressure. So $\frac{dk_1}{k_{-1}}$ represents the equilibrium probability that the reactant molecule has energy in the range from E to $E + dE$. Thus, $\frac{dk_1}{k_{-1}}$ can be expressed as *P(E)dE*. After all these notational changes, equation becomes the familiar expression for the thermal unimolecular rate constant,

$$k_{uni} = \omega \int_{E_0}^{\infty} \frac{k(E)P(E)dE}{\omega + k(E)} \tag{19}$$

According to the quantum mechanical Boltzmann distribution (Note that it is different from the Maxwell-Boltzmann distribution), *P(E)* can be expressed as below.

$$P(E_i) = \frac{g_i exp(^{-E_i}/_{k_B T})}{\sum_i g_i exp(^{-E_i}/_{k_B T})} = \frac{g_i exp(^{-E_i}/_{k_B T})}{Q} \qquad (20)$$

(where g_i is the degeneracy at energy E_i.)

If energy is assumed to be continuous, then the number of states $W(E)$ in the energy interval E to $E + dE$ is equivalent to g_i. If we divide $W(E)$ with dE, we can get the density of states $N(E)$. If we sum up all the number of W(E), we can get the total number of states $G(E)$ having energy in the range 0 to E. These $W(E)$, $N(E)$ and $G(E)$ are important terms when calculating unimolecular reaction rate constant and we will be discussing deeply in next section 4.

So now, the only mystery term that has to be cleared in equation (19) would be $k(E)$. Actually there are two quite different approaches. One is to consider the intramolecular motion of highly energized molecules, suggested by Slater in 1939. In this approach, we are assuming the explicit picture of a molecule as an assembly of harmonic oscillators and decomposition is assumed to occur when a critical coordinate (e.g., a bond length or bond angle) attains a critical displacement. This one would not be covered in this paper.

The other approach is based on statistical assumptions, so called RRK (Rice-Ramsperger-Kassel) theory. This RRK theory has been later followed by its extension, which is referred to as the RRKM (Rice-Ramsperger-Kassel-Marcus) theory. According to these theories, a molecule is assumed as a collection of coupled harmonic oscillators that can exchange energy freely under two main assumptions that

i. **All degenerate internal molecular states at energy E of the energized molecule A^* are accessible and will ultimately lead to decomposition products.**

ii. **Intramolecular Vibrational-energy Redistribution (IVR) of the energized molecule A^* occurs on a time scale much shorter than the lifetime of decomposition: $\tau = 1/k(E)$.**

Since a collection of molecules in RRK and RRKM is assumed as *microcanonical ensemble* (Only the degenerate states whose energy is equated to the fixed energy of the system have non-zero probabilities and those probabilities will be all the same; $P_i = 1/W$ where W is the degeneracy of the fixed energy level E_{system}), the assumption requires that each state have equal probability of decomposing so that a *microcanonical ensemble* will be still maintained during decomposition reaction. As a result, the unimolecular reaction rate constant will be described by only one time-independent rate constant $k(E)$ in equation (19). Such a unimolecular system obeys the Ergodic Principle of statistical mechanics. (i.e. all accessible microstates are *equiprobable* over a long period time**. RRK and RRKM are made in order to calculate this $k(E)$.**

4. RRK Theory

RRK theory was developed independently but nearly simultaneously by Rice and Ramsperger (1927), and Kassel (1928). Rice and Ramsperger developed *classical version of RRK theory* and Kassel developed *quantum version of RRK theory*, which will become identical in the limit of a large excitation energy *E*.

Classical version of RRK theory

The key idea in *classical version* is the probability that a molecule having *s*-classical oscillators with total energy of *E* has energy greater than or equal to E_0 in one chosen oscillator (critical oscillator leading to reaction). This probability is defined by the number of ways to attain this particular distribution divided by the total number of ways to distribute total energy *E* among the *s*-oscillators (i.e. $\frac{\text{one critical oscillator has energy} \geq E_0}{\text{total ways of distributing } E \text{ in s−oscillators}}$). The numerator is equated to the classical density of states in harmonic oscillator, i.e., *N*(*E*) and the denominator is total ways of combination where the critical oscillator contains energy $E_0 + E'$ and distributing the leftover energy $E – E_0 + E'$ in the remaining *s*-1 oscillators (refer to Appendix #1 for derivation of the classical density and sum of states: (A1-6) and (A1-5)). As a result, the probability for the critical oscillator (of the molecule having total energy of *E*) having energy greater than or equal to E_0 is as below.

$$\left[\int_{N(E'=0)}^{N(E'=E-E_0)} dN\, N\right] \Big/ N(E)$$

$$= \underbrace{\left[\int_0^{E-E_0} \frac{dE'}{h\nu}\left(\frac{(E-E_0-E')^{s-2}}{(s-2)!\prod_{i=1}^{s-1} h\nu_i}\right)\right]}_{\text{1-critical oscillator have energy} \geq E_0} \Bigg/ \underbrace{\frac{E^{s-1}}{(s-1)!\prod_{i=1}^{s} h\nu_i}}_{\text{total ways of distributing } E \text{ in } s\text{-oscillator}}$$

After integration, the above equation becomes as below

$$\text{Probability} = \left(\frac{E-E_0}{E}\right)^{s-1} \tag{21}$$

Thus, the rate constant *k*(*E*) is simply expressed as the multiplication between this probability and the vibrational frequency (unit: 1/s) for the critical oscillator, i.e.,

$$k(E) = \nu_{critical} \times \left(\frac{E-E_0}{E}\right)^{s-1} \ [1/s] \tag{22}$$

Quantum version of RRK theory

The basic idea in *quantum version* is very similar to that used for the classical version. However, in quantum theory, it is assumed that there are *s* identical oscillators in the molecule, all having frequency *v*. The energized molecule contains a total of *j*-quanta (i.e. total energy $E = j \cdot hv$). The critical oscillator must contain *m* quanta for reaction to occur ($E_0 = m \cdot hv$). Following this assumption combined with the key idea in *classical version*, the probability for particular distribution can be expressed as below.

$$\text{Probability} = \frac{\text{all cases in which a number of quanta in the critical oscillator ranges from } m \text{ to } j}{\text{total ways of distributing } j\text{– quanta in } s\text{– oscillators}}$$

The above equation can be also expressed as

$$\text{Probability} = \frac{G(E_{j-m} \text{ in } s\text{– 1 oscillators})}{W(E_j \text{ in s oscillators})}$$

Since,

$$W(E_j) = \frac{(j+s-1)!}{j!(s-1)!} \text{ and } G(E_j) = \frac{(j+s)!}{j!s!}$$

(see Appendix #2 for derivation)

As a result,

$$\text{Probability} = \frac{\frac{(j-m+s-1)!}{(j-m)!\,(s-1)!}}{\frac{(j+s-1)!}{j!\,(s-1)!}} = \frac{(j-m+s-1)!\,j!}{(j-m)!\,(j+s-1)!}$$

Since the rate constant $k(E)$ is simply expressed as the multiplication between this probability and the vibrational frequency for the critical oscillator,

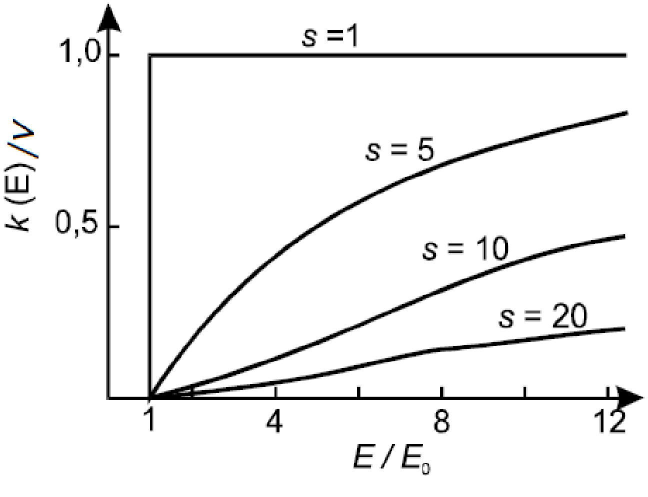
$$k(E) = \nu \times \frac{(j-m+s-1)!j!}{(j-m)!(j+s-1)!} \quad [1/\text{s}] \tag{23}$$

In the classical limit, where $j >> s$ and j-$m >> s$, the quantum RRK rate constant $k(E)$ becomes as below

$$k(E = jh\nu) = \nu \left(\frac{j-m}{j}\right)^{s-1} \quad [1/\text{s}] \tag{24}$$

using Stirling's approximation (Appendix #3).

As you can see, the equation (24) and (22) is same when $(h\nu)^{s-1}$ is multiplied to both the numerator and denominator in (24). From equation (22), we can say that the RRK rate constant depends on both the number of vibrational degrees of freedom and the energy in excess of E_0 (activation energy). If we express equation (22) visually for several s values, with y-axis of $k(\text{E})/\nu$ and with x-axis of E / E_0, this will be as below.



(Comparison of $k(E)$ between Lindemann-Hinshelwood (s=1) and classical RRK theory (s>1))

From the figure above, two important features can be found. First, with increasing excess energy, the rate constant increases towards its maximum value of *v* (which corresponds to energy independent rate constant k_2 in Lindemann-Hinshelwood theory). Second, for a particular value of total energy *E*, the rate of constant decreases with increasing number of *s*. These features are pretty intuitive in the sense that for larger molecule with larger number of vibrational modes, there are more ways to distribute the energy and hence less chance for energy to be localized in the critical mode (i.e. more stable the molecule becomes).

Now, if we apply this energy dependent $k(E)$ in equation (19) to get k_{uni}…

$$k_{uni} = \omega \int_{E_0}^{\infty} \frac{k(E)P(E)dE}{\omega + k(E)} = \frac{\nu \cdot e^{-E_0/RT}}{(s-1)!} \int_{E_0}^{\infty} \frac{\left(\frac{E-E_0}{RT}\right)^{s-1} \cdot e^{-\frac{E-E_0}{RT}} \cdot \frac{dE}{RT}}{1 + \frac{\nu}{\omega}\left(\frac{E-E_0}{E}\right)^{s-1}}$$

$$(\text{since } P(E)dE = \frac{dk_1}{k_{-1}} = \frac{1}{(s-1)!}\left(\frac{E}{k_B T}\right)^{s-1} e^{-E/k_B T}\left(\frac{dE}{k_B T}\right))$$

and if we replace

$$x = \frac{E-E_0}{RT} \quad \& \quad b = \frac{E_0}{RT}$$

we can get,

$$k_{uni} = \frac{\nu \cdot e^{-E_0/RT}}{(s-1)!} \int_0^{\infty} \frac{x^{s-1} \cdot e^{-x} \cdot dx}{1 + \frac{\nu}{\omega}\left(\frac{x}{b+x}\right)^{s-1}}$$

Recall that ω is the collision frequency. Thus, in the high-pressure limit ($\omega \to \infty$) and using the knowledge that $\int_0^{\infty} x^{s-1} \cdot e^{-x} \cdot dx = (s-1)!$ (Appendix #4), k_{uni} becomes the Arrhenius equation as below

$$k_{uni,\infty} = \nu \cdot e^{-E_0/RT} \tag{25}$$

Significant improvements have been made over the Lindemann-Hinshelwood theory by RRK theory. RRK theory gave reasonable agreement between experimental results and calculation. However, still, a value for s (i.e. the total number of vibrational modes in the molecule) was deviated from that calculated from RRK theory (e.g. one-fourth to two-thirds). Also, Arrhenius high-pressure thermal A-factors from experiments were 10^3 times larger than those derived from RRK theory (i.e. the frequency for the critical oscillator). These shortcomings of the RRK theory had later been overcome by RRKM theory.

5. RRKM Theory

The RRKM theory applied several minor modifications to the RRK model. These modification includes microcanonical transition state theory, explicit consideration on vibrational, rotational, and zero-point energies. After the reactant (molecule A) gets energy, the energized molecule A^* goes through isomerization or dissociation via the mechanism as below

$$A^* \xrightarrow{k(E)} A^\ddagger \rightarrow \text{Product(s)}$$

where $A^\ddagger$ represents the transition state of the reaction. In transition state theory, trajectories passing from A^* to $A^\ddagger$ (or vice versa) are assumed to pass through this transition state only once and this is also assumed in the RRKM theory. Also, the internal degrees of freedom of A^* and $A^\ddagger$ are designated as either active (energy can be exchanged freely between active modes during the reaction) or adiabatic (quantum state doesn't change during the reaction). For example, external rotational modes are considered to be adiabatic due to conservation of angular momentum (constant of motion), while the vibrational and internal rotational modes are considered to be active.

So from now on, we have to carefully treat the energies. First, in applications of RRKM theory, symmetric top approximation to both the energized molecule (A^*) and the transition state ($A^\ddagger$). As a result, the rotational energy-level expression for a rigid symmetric top would be as below (refer to p.181 from **Spectra of Atoms and Molecules** written by Peter F. Bernath)

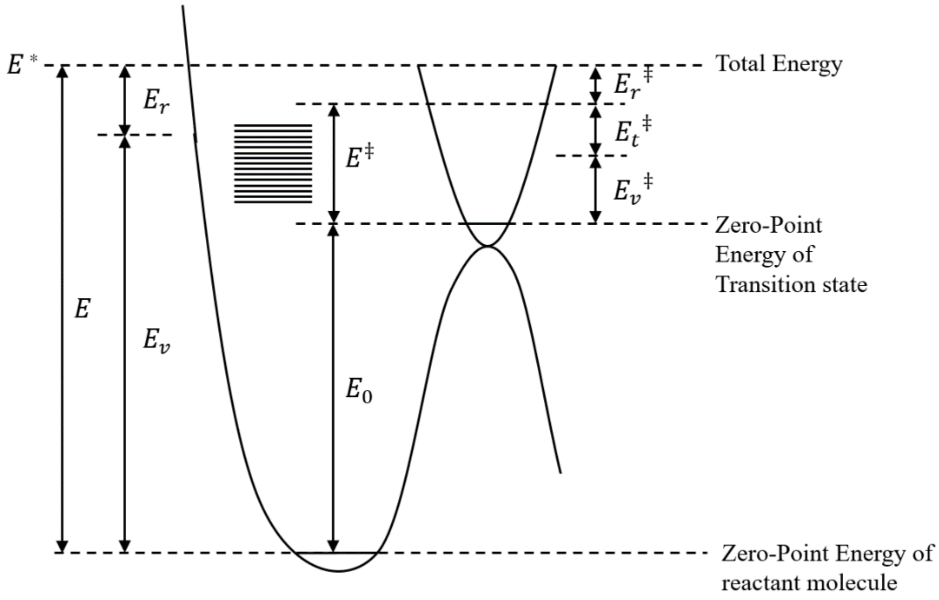
$$E_r(J, K) = \frac{J(J+1)\hbar^2}{2I_a} + \frac{K\hbar^2}{2}\left(\frac{1}{I_c} - \frac{1}{I_a}\right) \tag{26}$$

where J is the total angular momentum quantum number and K is the angular momentum quantum number along the molecular axis c. I_x is the moments of inertia on the axes that is labeled as x. (A coordinate system used here is *principal axis system*: Prolate symmetric tops: $I_c < I_a = I_b$; Oblate symmetric tops: $I_c > I_a = I_b$;)

The J-dependent term in equation 26 is assumed to be adiabatic, while K-dependent term can be treated as either adiabatic or active. In the case of K adiabatic, the rate constant depends on total energy, E, and J and K quantum number. In a simplified RRKM model, K quantum number is assumed to be active and thus E_r equals to J-dependent term only. The total energy E of the energized molecule can be treated as the sum of E_v (vibrational and internal rotational energy) and E_r (external rotational energy). Since molecular motion from A^* to $A^\ddagger$ involves a change in potential energy, the total energy of the transition state will be described as below.

$$E^\ddagger + {E_r}^\ddagger = E - E_0 \tag{27}$$

E_0 is the potential energy difference between A^* and $A^\ddagger$. $E^\ddagger$ is the sum of $E_v^\ddagger$ (the vibrational and internal energy of the transition state) and $E_t^\ddagger$. (the translational energy of the transition state during isomerization) Visualization of this energy diagram is illustrated in the figure below.



(Energy diagram for the RRKM theory)

The microcanonical transition state theory rate constant *k(E)* is given by

$$k(E) = \frac{G^\ddagger(E-E_0)}{hN(E)} \tag{28}$$

where $G^\ddagger$ refers to the sum of states in the transition state and *N* is the density of states in the reactant.

In the RRKM theory, the rate constant *k(E)* is given by

$$k(E) = \frac{G(E^\ddagger)}{hN(E_v)} \tag{29}$$

As you can see, the numerator in the equation 29 is the sum of states for the active degrees of freedom in the transition state and the denominator is the density of states for the active degrees of freedom in the reactant. Note that if equation A1-5 and A1-6 are used for $G\ (E^\ddagger)$ and $N(E_v)$, *k(E)* becomes equal to equation 22.

The RRKM rate constant can be also written as an explicit function of adiabatic rotational energy.

$$k(E, E_r) = \frac{1}{h}\frac{G(E^\ddagger)}{N(E-E_r)} \tag{30}$$

From equation 27, $E^\ddagger$ can be written as

$$E^\ddagger = E - E_0 - E_r{}^\ddagger = E_v + E_r - E_0 - E_r{}^\ddagger \tag{31}$$

In a simplified RRKM model mentioned above, since the external rotational modes (*J*-dependent term in equation 26) are assumed to be adiabatic, their angular momentum *L* will be conserved during the isomerization. By the way, *L* is described as below

$$L = \sqrt{J(J+1)}\hbar \tag{32}$$

Then from equation 31,

$$E_r - {E_r}^{\ddagger} = \frac{L^2}{2I_a} - \frac{L^2}{2I_a^{\ddagger}} = E_r\left(1 - \frac{I_a}{I_a^{\ddagger}}\right) \tag{33}$$

If we apply equation 33 into equation 30:

$$k(E, E_r) = \frac{G\left(E - \frac{I_a}{I_a^{\ddagger}}E_r - E_0\right)}{hN(E - E_r)} \tag{34}$$

Equation 34 is equivalent to

$$k(E_v, E_r) = \frac{G\left(E_v + E_r\left[\frac{I_a}{I_a^{\ddagger}}\right] - E_0\right)}{hN(E_v)} \tag{35}$$

In a more detailed and accurate treatment of external rotational energy, the RRKM rate constant is written as a function of total energy *E* and angular momentum quantum number *J*:

$$k(E, J) = \frac{G^{\ddagger}(E, J)}{hN(E, J)} \tag{36}$$

The *K*-dependent term in equation 26 is treated as an active and if this quantum number is considered in the rate constant calculation,

$$N(E, J, K) = N[E - E_r(J, K)] \tag{37}$$

$$G^{\ddagger}(E, J, K) = G^{\ddagger}[E - E_0 - E_r^{\ddagger}(J, K)] \tag{38}$$

$G^{\ddagger}(E,J)$ and $N(E,J)$ are found for *E* and *J* by summing over contributions from all possible values of *K:*

$$G^{\ddagger}(E, J) = \sum_{K=-J}^{J} G^{\ddagger}(E, J, K)$$

$$N(E, J) = \sum_{K=-J}^{J} N(E, J, K)$$

In this more detailed and accurate treatment of rotational energy, the total energy cannot be written as the sum of $E_v + E_r$, since the rotational energy changes with quantum number *K.*

Now, when it comes to determining an RRKM rate constant, we first need the information for calculating the sum and density of states in equation 36. These are the reaction total energy *E*, total angular momentum *J*, the reaction barrier E_0, the harmonic vibrational frequencies and moments of inertia for both the reactant and the transition state. Usually, *E*, *J*, and the reactants' moments of inertia and harmonic vibrational frequencies can be obtained from the experiment. However, the other information related with transition state is usually indirect and can be obtained from ab-initio calculation using computational chemistry software such as *Gaussian*. Determining the transition state's properties (E_0, $I_i^\ddagger$ and $v_i^\ddagger$) depends on the nature of the transition state and there are two general situations: (1) a saddle point exists between the reactants and the products, at which the transition state is located; (2) either no saddle point exists, as in the reverse reaction of barrier-less reaction (e.g. $CH_3 + H \rightarrow CH_4$), or the saddle point region is very flat (so you see multiple, usually very small, negative 2nd derivative vibrational frequencies). For the latter case, the transition state's position on the potential energy surface is energy or reaction coordinate dependent, which requires microcanonical variational transition state theory or Variational Reaction Coordinate Transition State Theory (VRC-TST) to find the proper submerged transition state.

Provided with this set of essential information, the next step is evaluating the sum of states for the transition state, $G^\ddagger(E,J)$, and the density of states for the reactant molecule, $N(E,J)$. The internal vibrational degrees of freedom are usually treated as quantum harmonic oscillators, and there are two major ways to calculate the sum and density. One way is to apply the accurate Whitten-Rabinovitch approximation (Whitten and Rabinovitch, *J. Chem. Phys.* 1964; Tardy et al., *J. Chem. Phys.* 1968) that will not be considered here. The other way is direct state counting using Beyer-Swinehart algorithm (Beyer and Swinehart, *Commun. Assoc. Comput. Machin. 1973*) on a computer. (refer to Appendix #5 for actual Matlab code and brief explanation of the principle)

Finally, using equation 36, we can finally obtain RRKM rate constant k(E) in equation 19!!

Appendix #1: Classical calculation of density and sum of states in harmonic oscillator

First, we need to think about the classical Hamiltonian of a single harmonic oscillator which is as below

$$H\left(\frac{dx}{dt}, x\right) = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2 + \frac{1}{2}4\pi^2\nu^2 m x^2$$

(since $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$)

If we replace the variables *x* and *t* with

$$q = \sqrt{m} \cdot x$$

$$p = \frac{dq}{dt}$$

then the classical Hamiltonian of a single harmonic oscillator will look like

$$H(p, q) = \frac{p^2}{2} + \frac{\lambda q^2}{2} \qquad \text{(A1-1)}$$

where

$$\lambda = 4\pi^2\nu^2$$

According to a theorem in classical statistical mechanics, the number of states for one degree of freedom with momentum *p* and coordinate *q* is

$$\text{The number of states} = \frac{dpdq}{h}$$

where $dp \cdot dq$ is the phase space volume associated with *p* and *q*. *h* is Planck's constant which is minimum phase space volume constrained by the uncertainty principle. For this reason, the number of states, *G*(*E*), the total phase space volume V_s divided by h^s where *s* refers to the degree of freedom.

$$G(E) = \frac{V_s}{h^s} = \frac{1}{h^s}\oint_{H=0}^{H=E} dp_1 \cdots dp_s dq_1 \cdots dq_s \qquad \text{(A1-2)}$$

In case of a single harmonic oscillator (i.e. a degree of freedom is one)

$$V_1 = \int_{H=0}^{H=E}\int dpdq \qquad \text{(A1-3)}$$

The integral in equation A1-3 is simply the area of an ellipse with regard to the equation of an ellipse from (A1-1) as below.

$$H\psi = E\psi = \left(\frac{p^2}{2} + \frac{\lambda q^2}{2}\right)\psi$$

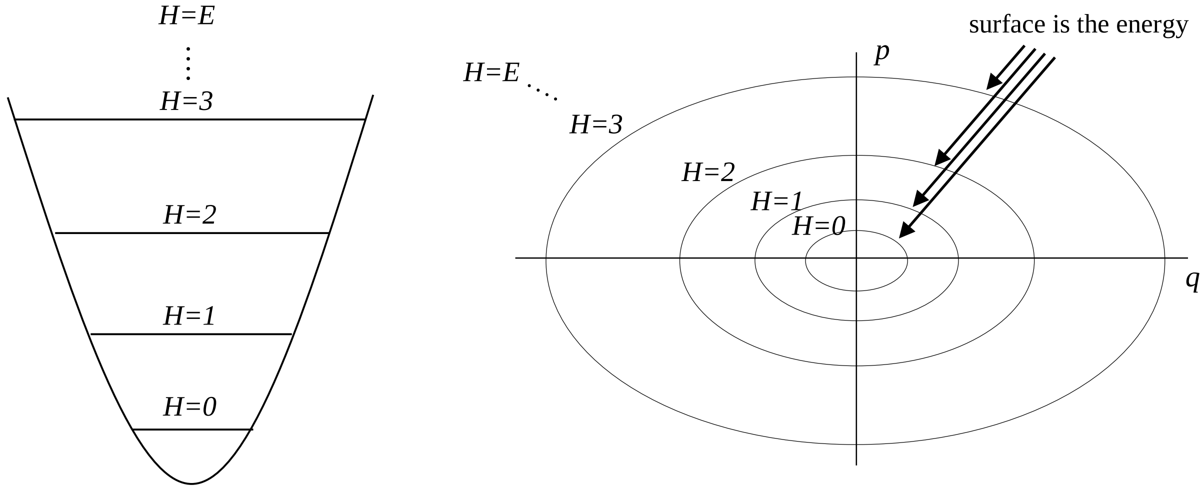
$$\therefore 1 = \frac{p^2}{2E} + \frac{\lambda q^2}{2E} \qquad \text{(A1-4)}$$

Since the area of an ellipse for ellipse equation $1 = \frac{x^2}{a^2} + \frac{y^2}{b^2}$ is $ab\pi$, the phase volume V_1 will be

$$V_1 = \pi \times \sqrt{2E} \times \sqrt{\frac{2E}{\lambda}} = \frac{E}{\nu}$$

and as a result, the classical sum of states is

$$G(E) = \frac{E}{h\nu}$$



(Visualization of a single harmonic oscillator)

Now, for s harmonic oscillators, the classical number of states is given by equation (A1-2) and the Hamiltonian for s harmonic oscillators is

$$H = \sum_{i=1}^{s} \left(\frac{{p_i}^2}{2} + \frac{\lambda_i {q_i}^2}{2} \right)$$

If one can notice that the above equation is the equation for a 2s-dimensional ellipsoid with semiaxes along p_i and q_i, the volume for this ellipsoid integrated from $H(p_i, q_i) = 0$ to $H(p_i, q_i) = E$ is…

$$V_s = \frac{E^s}{s! \prod_{i=1}^{s} \nu_i} \qquad \text{(A1-5)}$$

You might be curious of ‘s!’. But this factorial is for considering s indistinguishable oscillators.

Finally, using equation (A1-2),

$$G(E) = \frac{E^s}{s! \prod_{i=1}^{s} h\nu_i} \qquad \text{(A1-5)}$$

and due to the definition of the density of states, $N(E)$,

$$N(E) = \frac{dG(E)}{dE} = \frac{E^{s-1}}{(s-1)! \prod_{i=1}^{s} h\nu_i} \qquad \text{(A1-6)}$$

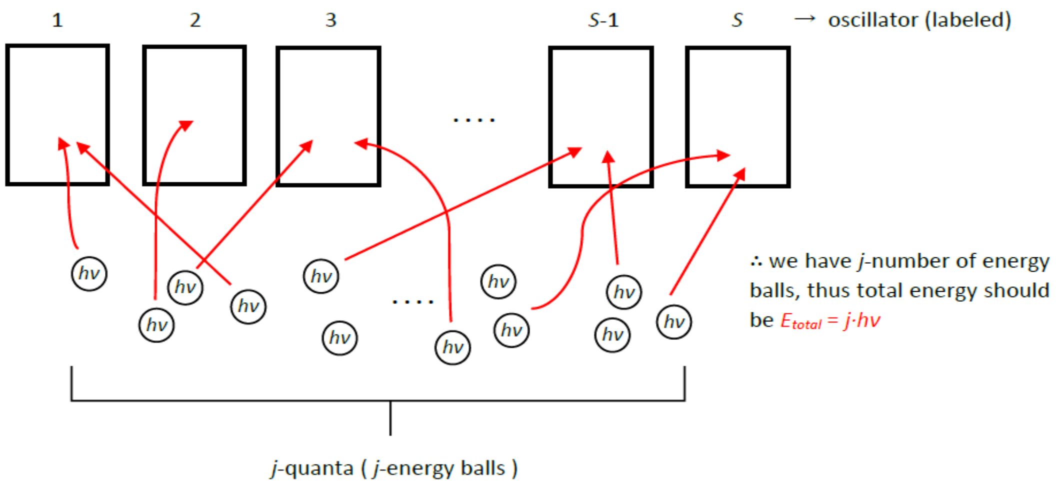
Appendix #2: Quantum calculation of number and sum of states in harmonic oscillator

Two assumptions are required on one certain molecule

i. All the frequencies in the molecule are identical (same v in each oscillators) (i.e. all energies are quantified, thus can be represented as $E_i = i\cdot hv$

ii. For **s**-oscillators each with frequency v, and total molecular energy above zero-point energy is $E_{total} = j\cdot hv$

e.g.

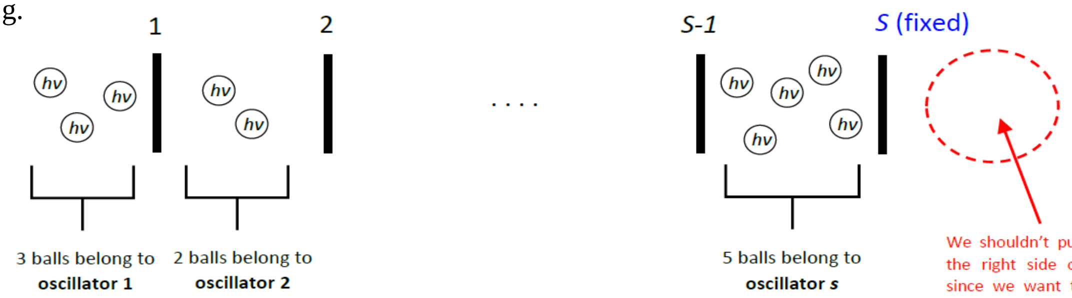


∴ we have j-number of energy balls, thus total energy should be $E_{total} = j\cdot hv$

(Distributing **j**-quanta in **s**-oscillators = $W(E_j)$)

Thus, when it comes to calculating $W(E_j)$, number of vibrational states at energy level $E_{total} = j\cdot hv$, we need to count all possible cases to distribute j-energy balls within **s**-oscillators as described in the figure above!! It is okay to put <u>whole *j* quanta only into '**oscillator 1**'</u> or <u>*j*/2 in '**oscillator 1**' and the other *j*/2 in '**oscillator *s***'</u>. Each case will be different vibrational state, but every state has same total molecular energy $E_{total} = j\cdot hv$ (Degeneracy!). We can use the concept of '*walls & balls*' to calculate this degeneracy $W(E_j)$. Let's say we have ***s*** walls and ***j*** balls. Assume that when balls are <u>*on the left side*</u> of the nearest wall, then those balls are <u>*all belong to that wall*</u>.

e.g.



We shouldn't put any balls on the right side of **oscillator *s***, since we want to distribute j-quanta (balls) with ***s***-oscillators without any leftovers!

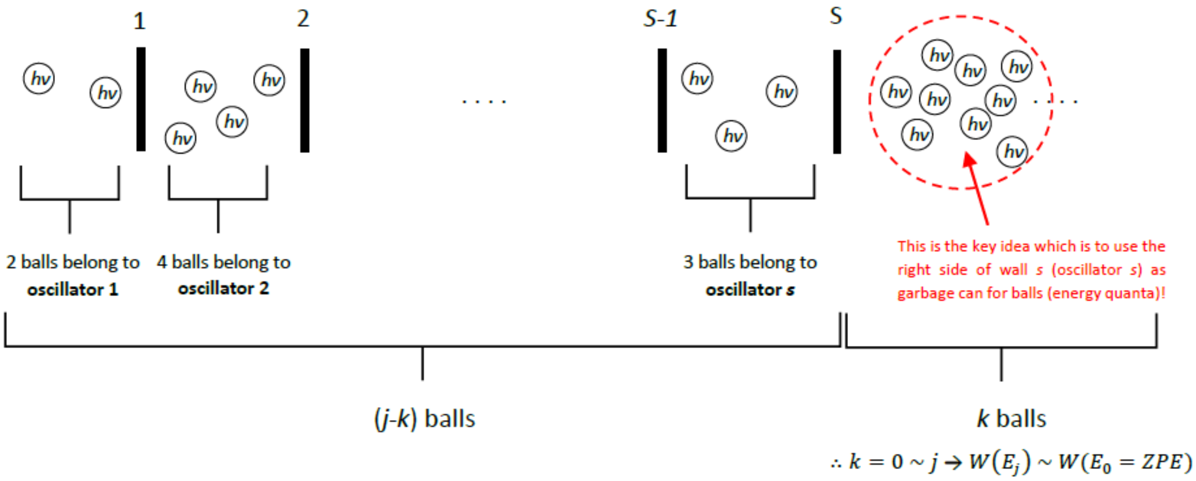
$$W(E_j) = \frac{(j + s \boxed{- 1})!}{j!\,(s - 1)!}$$

We don't want any ball on the right side of **oscillator *s***. So we will fix **oscillator *s*** and this came out as -1.

(Ordering j balls and s-1 walls and those balls and walls are indistinguishable)

Now, when it comes to $G(E_j)$, sum of vibrational states from energy level E_0 (= Zero Point Eenergy) to E_j (= $j \cdot hv$), the basic idea is almost same with the way we did as above using the concept of '*walls & balls*', but the main difference is not to fix the **wall *s*** (**oscillator *s***). Rather, we use the right side of **wall *s***.

e.g.



$$\sum_{i=0}^{j} W(E_i) = G(E_j) = \frac{(j+s)!}{j!\,s!}$$

So as summary, for the molecule which is consist of ***s*** number of oscillators and has total energy of $E_{total} = j \cdot hv$, number of states and sum of states would be as below.

$$W(E_j) = \frac{(j+s-1)!}{j!(s-1)!} \qquad \text{(A2-1)}$$

$$G(E_j) = \frac{(j+s)!}{j!s!} \qquad \text{(A2-2)}$$

Appendix #3: Quantum RRK rate constant using Stirling's approximation

1) Stirling's Approximation

$$\ln n! = \sum_{j=1}^{n} \ln j \approx \int_{1}^{n} \ln x dx = [x \ln x]_1^n = n \ln n - n - 0 + 1$$

$$\therefore \ln n! = n \ln n - n + 1$$

2) QRRK rate constant calculation

$$W_{\boldsymbol{tot}} = \frac{(n^* + s - 1)!}{n^*!\,(s-1)!} \quad \& \quad W^{\ddagger} = \frac{(n^* - n^{\ddagger} + s - 1)!}{(n^* - n^{\ddagger})!\,(s-1)!}$$

where….

$E_{tot} = \varepsilon^* = n^* h\nu$

$E_{act} = \varepsilon^{\ddagger} = n^{\ddagger} h\nu$

W_{tot} is the number of distributing n^* quanta in s normal modes.

$W^{\ddagger}$ is the number of distributing **<u>AT LEAST</u>** $n^{\ddagger}$ quanta (required activation energy) in certain normal mode. This equals to the number of distributing $n^* - n^{\ddagger}$ quanta in other s–1 normal modes.

Thus, we have to use $G(E) = \frac{(j+s)!}{j!s!}$ formula of A2-2 for 's–1 oscillators'

Then, probability for a particular oscillator that has at least $n^{\ddagger}$ quanta and all s-oscillators to have total energy (n^* quanta) is the ratio of $W^{\ddagger}/W_{tot} = P^{\ddagger} = [\mathrm{A}^{\ddagger}]/[\mathrm{A}^*]$

From equation 23,

$$\frac{(j - m + s - 1)!\,j!}{(j-m)!\,(j+s-1)!} \xrightarrow{corresponds\ to} P^{\ddagger} = \frac{W^{\ddagger}}{W_{\boldsymbol{tot}}} = \frac{(n^* - n^{\ddagger} + s - 1)!\,n^*!}{(n^* + s - 1)!\,(n^* - n^{\ddagger})!}$$

In the classical limit, where $j >> s$ and $j - m >> s$, $\frac{(j-m+s-1)!j!}{(j-m)!(j+s-1)!}$ can be approximated to $\left(\frac{j-m}{s}\right)^{s-1}$ using ***Stirling's Approximation***

$$\ln P^{\ddagger} = \ln[(n^{*} - n^{\ddagger} + s - 1)!] + \ln(n^{*}!) - \ln[(n^{*} + s - 1)!]$$

$$= (n^{*} - n^{\ddagger} + s - 1)\ln(n^{*} - n^{\ddagger} + s - 1) - n^{*} + n^{\ddagger} - s + 1 + 1 + (n^{*}\ln n^{*} - n^{*} + 1) - \big((n^{*} + s - 1)\ln(n^{*} + s - 1) - n^{*} - s + 1 + 1\big) - \big((n^{*} - n^{\ddagger})\ln(n^{*} - n^{\ddagger}) - n^{*} + n^{\ddagger} + 1\big)$$

$$= (n^{*} - n^{\ddagger} + s - 1)\ln(n^{*} - n^{\ddagger} + s - 1) + n^{*}\ln n^{*} - (n^{*} + s - 1)\ln(n^{*} + s - 1) - (n^{*} - n^{\ddagger})\ln(n^{*} - n^{\ddagger})$$

Since $n^{*} - n^{\ddagger} \gg s - 1$ ($j \gg s$ & $j - m \gg s$),

($(a + x)\ln(a + x) \approx a\ln a + x(1 + \ln a)$ when $x \ll a$, do *taylor expansion* and take the first two terms)

$$\approx (n^{*} - n^{\ddagger})\ln(n^{*} - n^{\ddagger}) + (s - 1)(1 + \ln(n^{*} - n^{\ddagger})) + n^{*}\ln n^{*} - n^{*}\ln n^{*} - (s - 1)(1 + \ln n^{*}) - (n^{*} - n^{\ddagger})\ln(n^{*} - n^{\ddagger})$$

$$= (\mathrm{s} - 1)(\ 1 + \ln(n^{*} - n^{\ddagger}) - 1 - \ln n^{*}) = (s - 1)\ln\left(\frac{n^{*} - n^{\ddagger}}{n^{*}}\right)$$

$$\therefore \ln P^{\ddagger} \approx (s - 1)\ln\left(\frac{n^{*} - n^{\ddagger}}{n^{*}}\right)$$

$$P^{\ddagger} \approx \left(\frac{n^{*} - n^{\ddagger}}{n^{*}}\right)^{s-1} = \left(\frac{j - m}{s}\right)^{s-1}$$

Appendix #4: Gamma function

$$Gamma\ function \int_0^{\infty} x^{s-1}e^{-x}dx = ?$$

$$\int_0^{\infty} x^{s-1}e^{-x}dx + \int_0^{\infty} -\frac{x^s}{s}e^{-x}dx = \left[\frac{x^s e^{-x}}{s}\right]_0^{\infty} = 0$$

$$\therefore \int_0^{\infty} x^{s-1}e^{-x}dx = \frac{1}{s}\int_0^{\infty} x^s e^{-x}dx$$

$$\int_0^{\infty} x^{s-2}e^{-x}dx = \frac{1}{s-1}\int_0^{\infty} x^{s-1}e^{-x}dx$$

$$\int_0^{\infty} x^{s-3}e^{-x}dx = \frac{1}{s-2}\int_0^{\infty} x^{s-2}e^{-x}dx$$

$$\int_0^{\infty} x^{s-4}e^{-x}dx = \frac{1}{s-3}\int_0^{\infty} x^{s-3}e^{-x}dx$$

$$\vdots$$

$$\int_0^{\infty} xe^{-x}dx = \frac{1}{2}\int_0^{\infty} x^2e^{-x}dx$$

$$\int_0^{\infty} e^{-x}dx = \int_0^{\infty} xe^{-x}dx$$

$$\therefore 1 \cdot 2 \cdot 3 \cdots (\mathrm{s}-1)\int_0^{\infty} e^{-x}dx = (\mathrm{s}-1)! = \int_0^{\infty} dx \cdot x^{s-1}e^{-x}$$

$$\therefore \int_0^{\infty} dx \cdot x^{s-1}e^{-x} = (\mathrm{s}-1)!$$

Appendix #5: Beyer-Swinehart algorithm with Matlab code

```
function [N]=Beyer_Swinehart_Algorithm(v,s,n)
%  COUNT COMPUTES THE NUMBER OF PARTITIONS OF AN INTEGER
%  RESTRICTED TO v FOR INTEGERS IN THE RANGE 1 TO n.
%  INPUT:  s -- A POSITIVE INTEGER (total number of vibrational modes)
%          v -- AN ARRAY OF s POSITIVE INTEGERS (vibrational mode)
%          n -- AN INTEGER LARGER THAN THE MAXIMUM VALUE IN v (Energy)
%  OUTPUT: N -- AN ARRAY OF n INTEGERS, WHERE P(M) IS THE
%                 NUMBER OF PARTITIONS OF M RESTRICTED TO v.
%  INITIALIZE N
   N =zeros(n,1);
%  EACH PASS THROUGH THE OUTER LOOP BELOW TRANSFORMS N FROM
%  PARTITIONS RESTRICTED TO v(1), ..., v(i-1) TO
%  PARTITIONS RESTRICTED TO v(1), ..., v(i).
   for i = 1 : s;
   j = v(i);
   jp1 = j + 1;
   N(j) = N(j) + 1;
      for m = jp1 :1: n;
       mmj = m - j;
       N(m) = N(m) + N(mmj);
      end
   end
end
```

How does this algorithm work? This algorithm can cover all the possibilities as below.

i. m $< v_i$, $N_{v_1,\cdots,v_{i-1}}(m) = N_{v_1,\cdots,v_{i-1},v_i}(m)$
ii. m $= v_i$, $N_{v_1,\cdots,v_{i-1}}(m) + 1 = N_{v_1,\cdots,v_{i-1},v_i}(m)$
iii. m $> v_i$, $N_{v_1,\cdots,v_{i-1}}(m) + N_{v_1,\cdots,v_{i-1},v_i}(m - v_i) = N_{v_1,\cdots,v_{i-1},v_i}(m)$

v_1	v_2	v_3	$\cdots$	v_{i-1}	v_i
$N_{v_1,\cdots\cdots,v_{i-1}}(m)$					0
					0
					$\cdots$
					0
$N_{v_1,\cdots\cdots,v_{i-1},v_i}(m - v_i)$					0
					$\cdots$
					0
					1
					$\cdots$
					1
					$\cdots$
					$n_{v_i,max} - 1$
					$\cdots$
					$n_{v_i,max} - 1$
					$n_{v_i,max}$
					$\cdots$
					$n_{v_i,max}$

$$\therefore N_{v_1,\cdots\cdots,v_i}(m) = N_{v_1,\cdots\cdots,v_{i-1}}(m) + N_{v_1,\cdots\cdots,v_{i-1},v_i}(m - v_i)$$