# Transition State Theory with Tsallis Statistics

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**Abstract:** We discuss the rate of an elementary chemical reaction. We use the reaction path and especially its saddle point on the potential energy surface. The reaction path connects reactant and product of a reaction over the transition state (TS). Usually, the TS is assumed near or at the single saddle point of the reaction path. By means of comparison of the statistics of states at the reactant and at the TS, one can estimate the reaction rate by the Eyring theory. We propose to use the Tsallis statistics at the TS, a statistics of seldom accidents. Thus, we propose to generalize the well known Boltzmann-Gibbs statistics which is the limiting case of the Tsallis statistics. We use features of this non-extensive thermo-statistics. The basic properties of the statistics are employed to derive (approximated) partition functions, and they are applied on reaction rates. The approximation includes a factorization of the partition functions. The theory is applied to HCN isomerization to HNC, and to the reaction $H_2+CN \rightarrow H+HCN$. It allows an accordance with experimental estimations of the reaction rates.

# Introduction

Reactive events are the heart of any chemistry. The need for the computation of the reactive propensities of chemical species is ubiquitous in physical chemistry. The detailed, quantitative understanding of gas-phase chemistry is not yet fully within our grasp. Such understanding should be based on first principles calculations of the potential energy, or the free energy, along a "reaction coordinate". Transition state theory (TST) is a cornerstone of reaction rate theory and it is taught in elementary texts in chemistry and biochemistry. The literature on TST is vast, and cannot be listed here. The concept dates back to the 1930s[1,2] and its modern version with many improvements, including treatments of variational effects, has been reviewed in several articles.[3,4,5]

The original version of the theory applies to so-called activated reactions. For such reactions one treats an energy barrier on a potential energy surface (PES) which separates the reactants and products, and the top of the barrier is usually termed the transition state (TS). It is assumed to be near or at the saddle point of index one.[6] It should hold that the motion of the nuclei occurs on the Born-Oppenheimer PES under electronic adiabaticity of the reaction. The reaction rate, $k$, is written in the Arrhenius form[7]

$$k = A\mathrm{e}^{-\Delta E/k_B T} \ .$$

$\Delta E$ is the barrier height. Eyring[1] proposed to determine the prefactor $A$ by the partition functions of reactant and TS. This allowed a quantum mechanical formulation. Thus, current TST obtains the value of the rate constant and its temperature dependence on the statistical properties of reactant and TS. It is this power and simplicity of the theory that are responsible for its widespread use. The use of statistics avoids emphasis on the details of the molecular dynamics and the use of the TS requires only a minimal knowledge of the PES. The theories require local information about the PES. They circumvent the dimensionality dilemma for medium-sized or large molecules: it is impossible to fully calculate their PES. Additionally, it is most important that the parameters of the theory can be related to experimental observables - thermodynamic data in particular. However, the kind of statistics used may be carefully determined.

Closely related to TST, and often an extension of it, is the concept of the Intrinsic Reaction Coordinate (IRC)[8,9] or its equivalent formulation: reaction path (RP).[10,11] The IRC concerns elementary reactions. The IRC is the steepest descent from TS to reactant. (It always exists if the TS is exactly the SP of the PES.) However, there are also other concepts for the definition of the reaction path, like the Newton trajectory,[12,13] or the gradient extremal,[14,15] see ref.[16] for a review. The RP identifies a TS with reactant (or with product) and the potential energy along the pathway results in important dynamical extensions of TST, including various treatments of tunneling inclusion of "curvature effects", "corner-cutting", etc. These extensions of TST have been incorporated in very general and rigorous form in the Reaction Path Hamiltonian.[17] Thus, the concept of the RP of a PES is the usual approach to the theoretical kinetics of chemical systems.[18]

The simplicity of TST mentioned above is clear if one considers the alternative approach, which is scattering theory. In this approach much if not all of the PES is needed and this alone is far more information and thus requires much more computational effort to obtain than the information which is needed to apply TST. This already applies throughout to elementary reactions. Indeed, usually a reduced dimensionality approach is used.[19] There are numerous examples in the literature of deviations and failures of TST[20] and space does not permit an exhaustive review of these. Instead we give a sampling of notable examples: Deviations from TST have been discovered as a result of the application of scattering theory to the study of reaction dynamics since the 1960s. An early example of non-TS dynamics was reported for the triatomic reaction H + ICl where the product HCl was formed with a bimodal distribution of internal ro-vibrational energies.[21] A recent and detailed study of the analogous H + FCl reaction was reported by Sayos et al.[22] The failure of TST is not too surprising since at energies well above the TS there is less justification for the assumption that the dynamics will be governed by the (static) RP. Such deviations have been seen numerous times now in dynamical calculations. Besides direct "failure of TST",[23] there is usually given only a coarse agreement of TST with the experiment: $\sim$30% mean reasonable agreement, already for the variational TST.[24] (Overall, ... "the validity of the TST has not yet been really proved and its success seems to be mysterious." It is cited after an older reference.[25])

For any physical variable that is function F($\omega$) with $\omega \in \Omega$, the phase space, we can find the mean value with respect to the distribution $P$

$$<F>_{\mathbf{P}} = \int_{\Omega} F(\omega) \, d\, P(\omega) \ .$$

The main physical postulate of statistical physics, which connects theoretical constructions with experimental observations is that for a large system and certain classes of physical variables $F$, the values of $F$ measured experimentally almost coincide with their mean values $<F>_P$ with respect to a suitable probability distribution $P$ on $\Omega$.[26] The question is: "What is a suitable distribution?" In the general case, the so-called nonequilibrium case, when the system as a whole changes in time, the description of such a distribution is a very complicated problem.

Certainly the existence of a vast literature to TST raises the question "why should there be still another paper on the theoretical foundations of TST, what new can it possibly add?" The idea of this article is to use a distribution at the TS which describes non-equilibrium states, the Tsallis distribution.[27,28,29] One can (approximately) calculate partition functions for the Tsallis distribution, which deviate from the partition functions for the Boltzmann distribution. The deviation goes with the Tsallis parameter $q$: for $q < 1$ we obtain smaller, for $q > 1$ we obtain larger values of the partition functions. Thus, with a change to a Tsallis description of the TS, we have the possibility to better adapt the reaction rates of Eyrings TST to measured rates.

## Distribution and Partition Functions:

### Boltzmann-Gibbs Distribution

We repeat some fundamentals. The Boltzmann distribution is the probability of the dominant macro state. The probability to find the system in state $i$ (to energy value $E_i$) is

$$p_i = e^{-\beta E_i}/Z = \frac{e^{-\beta E_i}}{\sum_j e^{-\beta E_j}} \ . \tag{1}$$

$Z$ is the factor of normalization

$$Z = \sum_j p_j = \sum_j \mathrm{e}^{-\beta E_j} \ . \tag{2}$$

(The capital letter $Z$ is used because the German name is "Zustandssumme".) The sum over states is the sum over all micro states $j$ which the system can take over. It depends on the temperature by the inverse relation $\beta = 1/k_B T$, where $k_B$ is the Boltzmann constant $1.38065 \cdot 10^{-23} \, J \, K^{-1}$. For $N$ particles, or $N$ degrees of freedom of a molecule, the density of states is a function which counts the micro states in a special range of the energy. Consequently, the probability that the system is in a macro state with energy $E_i$ is the product of $N$ Boltzmann distributions.

$$Z_N = \sum_j \mathrm{e}^{-\beta(E_j^{(1)} + \dots + E_j^{(N)})} \propto \sum_j \mathrm{e}^{-\beta E_j^{(1)}} \cdots \sum_j \mathrm{e}^{-\beta E_j^{(N)}} = \left( \sum_j \mathrm{e}^{-\beta E_j} \right)^N \ , \tag{3}$$

thus it is exactly $Z_N = Z^N$ if the $N$ degrees of freedom are independent. We may assume the Boltzmann weighted mean value of a state function $F(j)$ for the expectation value weighted even by the Boltzmann distribution - like it is the usual way in stochastic

$$<F>_{\mathbf{B}} = \sum_j F(j)\, p_j = \frac{1}{Z} \sum_j F(j)\, \mathrm{e}^{-\beta E_j} \ .$$

**Tsallis Statistics**

We give a concise summary of a Tsallis statistics.[30,31,32] The starting point of the Tsallis theory is a modified distribution of the probability (of the Boltzmann distribution $p_i$) which now depends on a parameter $q$. In the limit $q \to 1$ this distribution is the Boltzmann-Gibbs distribution. It means we search for a function $f_q(x) = \mathrm{e}_q^x$ with $f_1(x) = \mathrm{e}^x$. We define the generalized Exponential function and the generalized Logarithm function (for $q$ near 1) being mutually inverse functions

$$\exp_q(x) = \begin{cases} (1 + (1-q)x)^{\frac{1}{1-q}} & \text{for } 1 + (1-q)x > 0 \\ 0 & \text{for } 1 + (1-q)x \leq 0, \end{cases} \tag{4}$$

and

$$\ln_q(x) = \frac{1}{1-q}(x^{q-1} - 1) \ . \tag{5}$$

For the definitions we have $\lim_{q \to 1} \exp_q(x) = \exp(x)$ and $\lim_{q \to 1} \ln_q(x) = \ln(x)$, as expected. The generalizations go back to Euler, and there are many other possibilities.[33] The Tsallis

theory is based on a generalization of the definition of entropy.

$$S_q = k\frac{1 - \sum_{j=1}^{W} p_j^q}{q - 1} , \qquad W \geq 1 , \quad \sum_{j=1}^{W} p_j = 1 ,$$

$k$ is a positive constant (with $k = k_B$ at $q = 1$), $W$ is the number of states of the system at an energy for the probability set $\{p_j\}$, $j = 1, ..., W$. A property of the generalized q-entropy is its nonextensivity.

Now we generalize the distribution of the energy. A discrete probability distribution is

$$p_{q(i)} = \frac{1}{Z_q}e_q^{-\beta E_i} = \frac{1}{Z_q}[1 - (1 - q)\beta E_i]^{\frac{1}{1 - q}} \tag{6}$$

with

$$Z_q = \sum_{j}^{W} e_q^{-\beta E_j} = \sum_{j}^{W}[1 - (1 - q)\beta E_j]^{\frac{1}{1 - q}} . \tag{7}$$

The definition (6) is the second choice of a possible Tsallis distribution. It has still some unfamiliar consequences.[34] However, it is not as complicate as the third choice.[34] In Fig.1 we compare the Boltzmann-Gibbs statistics (case q=1), and the Tsallis statistics (6) with $q = 0.875$, for values $\beta E_j = 0.7\,j$, with $j = 0, 1, \cdots, 10$. The gray bars are the usual Boltzmann-Gibbs probabilities, where the red bars (in color), or dark bars (in black and white), are Tsallis probabilities. States are calculated from $j = 0$ to $j = 10$ only, as well as the sum over states.
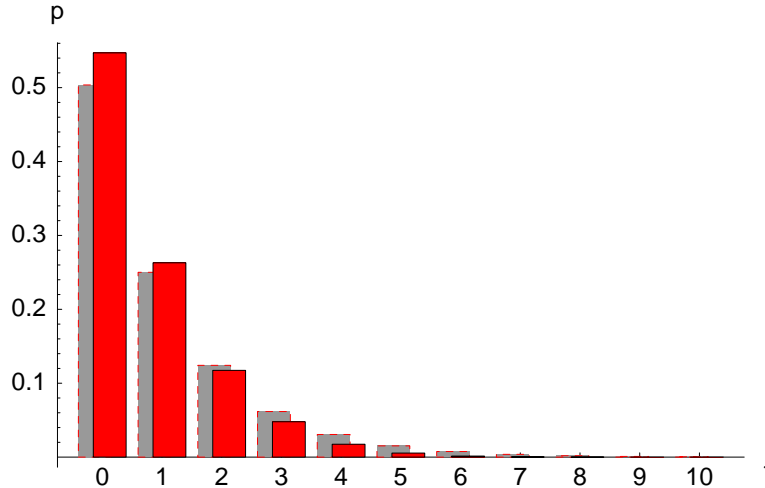


**FIGURE 1**. Comparison of probability distributions, gray: Boltzmann, red: a Tsallis distribution.

# The partition functions for molecules

One assumes in the classical case that the energy of a molecule can be approximately separated into translational, rotational, vibrational and electronic exitations, because for the single parts of the energy in the partition functions, we get a product in the exponential function. With

$$E_j = E_{trans} + E_{rot} + E_{vib} + E_{electr}$$

we obtain

$$Z_j = Z_{trans}\, Z_{rot}\, Z_{vib}\, Z_{electr} \ .$$

The different energies can be taken from Quantum mechanics, from solutions of the Schrödinger equation of the corresponding problem. Thus we can calculate the different sums of states. How does the case for the q-distribution change? If $q \neq 1$ we cannot further assume that single parts of translation, rotation and vibration factorize, because we do not have a simple exponential function like in the classical case (because of the non-extensivity). However, we will further approximate the full partition function by a product of the single sums over states, and we will just newly calculate the single sums over states of translation, or rotation, or vibration, by the Tsallis statistics.

## Sum over states for translation: classical calculation

We separate the 3-dimensional movement of translation of the center of mass into three Cartesian components. We take the approximation of the energy states of a one-dimensional particle in a box (with length $L$) for every direction. Our notation is fair standard. The energy is $E_j = \frac{j^2 h^2}{8mL^2}$, $j = 1, 2, \cdots$ are the state numbers, $h$ is the Planck constant, and $m$ is the particle mass. We approximate the discrete sum by a continuous integral and get

$$Z_{(1)}^{trans} = \sum_{j=0}^{\infty} \mathrm{e}^{-\beta E_j} \approx \int_0^{\infty} \mathrm{e}^{-\beta E(j)} \mathrm{d}j = \int_0^{\infty} \mathrm{Exp}\left(-\frac{\beta j^2 h^2}{8mL^2}\right) \mathrm{d}j = \frac{L}{h}\sqrt{\frac{2\pi m}{\beta}} = \frac{L}{\Lambda}$$

with the thermal de Broglie-wavelength

$$\Lambda = h\sqrt{\frac{\beta}{2\pi m}} \ .$$

We can suppress the quantization of energy in the approximation, because the energy differences $E_i$ and $E_{i+1}$ are very small for a large box length, $L$, already at room ambient

temperature, in comparison to $\beta = 1/k_B T$.

The partition function for three dimensions factorizes into the product of one-dimensional cases. For the Cartesian space we may have three for a molecule. Every energy state $E_i$ is the sum of the three parts deriving from the three degrees of freedom $E^{trans}_{i(3)} = E_i(1) + E_i(2) + E_i(3) = 3E_i$ , and the sum of translation states is the 3-times product of one-dimensional sum over translational states.

$$Z^{trans}_{(3)} = \sum_{i=0}^{\infty} e^{-3\beta E_i} \approx \left( \int_0^{\infty} e^{-\beta E(i)} di \right)^3 = \frac{V}{\Lambda^3} \tag{8}$$

with the volume $V$ of the container to which the molecule is confined.

**Sum over states for translation: q-generalized case**

Now we can calculate the partition functions using the Tsallis distribution, $p_q$. First we treat the q-translation sum in one dimension. We can go on like in the classical case. We use the distribution of the energy in $\boxed{\text{the case } q > 1}$. We find

$$Z^{trans}_{1<q} = \int_0^{\infty} (1 - (1-q)\beta E_j)^{\dfrac{1}{1-q}} \, dj = \int_0^{\infty} \left( 1 - (1-q)\beta \frac{j^2 h^2}{8mL^2} \right)^{\dfrac{1}{1-q}} \, dj \; .$$

Transforming $j$ to $y$ leads to

$$= \sqrt{\frac{8mL^2}{\beta h^2}} \int_0^{\infty} (1 - (1-q)y^2)^{\dfrac{1}{1-q}} dy = \frac{2L}{\Lambda \sqrt{\pi}} \underbrace{\int_0^{\infty} (1 - (1-q)y^2)^{\dfrac{1}{1-q}} dy}_{q-\text{integral from appendix with } y=r \text{ and } n=1} \; .$$

With $\Gamma(\frac{1}{2}) = \sqrt{\pi}$ we get

$$Z^{trans}_{1<q<3} = \frac{L}{\Lambda(q-1)^{1/2}} \frac{\Gamma(\dfrac{1}{q-1} - \dfrac{1}{2})}{\Gamma(\dfrac{1}{q-1})} \; . \tag{9}$$

The restriction $q < 3$ derives from the range of existence of the $\Gamma$-integral. The case $q \geq 3$ produces a divergent integral. $\boxed{\text{The case } 0 < q < 1}$ analogously develops with a somewhat modified substitution, see appendix, and we get

$$Z^{trans}_{q<1} \approx \frac{2L}{\Lambda\sqrt{\pi}} \int_0^{\sqrt{1/(1-q)}} (1 - (1-q)y^2)^{\frac{1}{1-q}} \, dy \tag{10}$$

$$= \frac{L}{\Lambda (1-q)^{1/2}} \frac{\Gamma(\frac{1}{1-q} + 1)}{\Gamma(\frac{1}{1-q} + \frac{3}{2})} \; .$$

## q-translation partition function of a molecule

In the general case we have $N$ nuclei in 3-space, thus 3N degrees of freedom. Only three degrees of freedom for a translation concern the center of mass of the molecule. The PES of the molecule, $V(\mathbf{x})$, is translationally invariant. Thus, it cancels out. The remaining q-integral goes over three dimensions. In a box with lengths $L_i$, $i = 1, 2, 3$, correspondingly, we have with coordinates $x_i$ and conjugate momenta $p_i$

$$Z_{q(3)}^{trans} = \frac{1}{h^3} \int_0^{L_1} \cdots \int_0^{L_3} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(1 - \frac{(1-q)\beta}{2m} \sum_{i=1}^3 p_i^2 \right)^{\frac{1}{1-q}} dp_1 \ldots dx_3$$

$$= \frac{L_1 L_2 L_3}{h^3} \left(\sqrt{\frac{2m}{\beta}}\right)^3 \underbrace{\int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(1 - (1-q)[y_1^2 + y_2^2 + y_3^2]\right)^{\frac{1}{1-q}} dy_1 dy_2 dy_3}_{q-\text{integral from appendix with } n=3}$$

$$= \frac{V}{\Lambda^3} \cdot \begin{cases} \left(\dfrac{1}{q-1}\right)^{\frac{3}{2}} \dfrac{\Gamma(\dfrac{1}{q-1} - \dfrac{3}{2})}{\Gamma(\dfrac{1}{q-1})} & \text{for } 1 < q < 1 + \frac{2}{3} \\[2em] \left(\dfrac{1}{1-q}\right)^{\frac{3}{2}} \dfrac{\Gamma(\dfrac{1}{1-q} + 1)}{\Gamma(\dfrac{1}{1-q} + \dfrac{5}{2})} & \text{for } 0 < q < 1 \; . \end{cases} \tag{11}$$

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad}_{A^{trans}(3, q)}$$

If we use the symbol $A^{trans}(3, q)$ for the $q$-factor, we may write the q-translational sum over states as a product of the classical translational partition function, and the $q$-factor

$$Z_q^{trans} = Z^{trans} \cdot A^{trans}(3, q) \; . \tag{12}$$

In the classical case $q = 1$ we get $A_{trans}(3, q) = 1$, because for $q \to 1$ we can use the approximation of the Gamma-function for large arguments $\dfrac{\Gamma(x + a)}{\Gamma(x + b)} \approx x^{(a-b)}$, and we get the classical translational sum.

## Classical sum over rotational states: linear molecule

The classical sum over rotational states of a linear molecule approximately uses the rotational levels of a rigid rotator, $\quad E_j = \dfrac{\hbar^2}{2I}j(j + 1) = hcBj(j + 1)$ with $j = 0, 1, 2, \ldots$, and $I$ is the moment of inertia, which is to be calculated by bond lengths and atomic masses

of the molecule. $B$ is the rotational constant: it is $B = \dfrac{h}{8\pi^2 cI}$. The rotations of a linear molecule are $(2j+1)$-times degenerate. For each value of $j$, there are $2j+1$ possible states of the same energy. Then we have the classical the partition function

$$Z_{(2)}^{rot\,lin} = \sum_{j=0}^{\infty} (2j+1)\mathrm{e}^{-\beta E_j} \ . \tag{13}$$

In an approximation, we can again replace the summation by an integral. The error is small, if the temperature is high enough. It happens if $hcB(j^2 + j)/k_B T \ll 1$. Then the energy levels are so dense that we can assume that they are continuously smeared. The critical temperature may be $T \geq 10\frac{hcB}{k_B}$ (it is $20\,\mathrm{K}$ for the molecule HCN).

$$Z_{(2)}^{rot\,lin} \approx \int_0^{\infty} (2j+1)e^{-\beta E(j)}\mathrm{d}j = \int_0^{\infty} (2j+1)e^{-hc\beta B(j^2+j)}\mathrm{d}j = \frac{1}{hc\beta B} \ . \tag{14}$$

Note, for homonuclear molecules we still have to reduce the doubly counted states by a symmetry number $\sigma = 2$.[35] If one strives for an exact approximation of the sum over rotational states, one can use the Euler-Maclaurin formula for the sum[36]

$$\sum_{i=a}^{\infty} f(i) = \int_a^{\infty} f(i)\mathrm{d}i + \frac{f(a)}{2} - \frac{f'(a)}{12} + \frac{f^{(3)}(a)}{720} - \frac{f^{(5)}(a)}{30240} + \frac{f^{(7)}(a)}{1209600} - \cdots \ . \tag{15}$$

It leads to the partition function under any temperature

$$Z_{(2)}^{rot\,lin} = \frac{1}{hc\beta B} + \frac{1}{3} + \frac{hc\beta B}{15} + \frac{4(hc\beta B)^2}{315} - \frac{1641(hc\beta B)^3}{1209600} + \cdots \ . \tag{16}$$

**Classical sum over rotational states: non-lineare molecule**

In the general case, the molecule has three different moments of inertia, $I_1, I_2$ and $I_3$. They can be calculated by the geometry of the molecule and the tensor of inertia. The rotational levels cannot be given in a simple form. However, a classical approximation holds with a good exactness:

$$Z_{(3)}^{rot} = \sqrt{\pi} \left(\frac{1}{hc\beta B_1}\right)^{1/2} \left(\frac{1}{hc\beta B_2}\right)^{1/2} \left(\frac{1}{hc\beta B_3}\right)^{1/2} \ . \tag{17}$$

**Sum over rotational states: q-generalized sum for linear and nonlinear molecules**

We calculate the q-rotational partition function[37] of a lineare molecule using the q-distribution. Again, we replace the sum by an integration. (In the general case we may use the Euler-Maclaurin formula for the sum.)

$$
\begin{aligned}
Z_{q(2)}^{rot\,lin} &= \sum_{j=0}^{\infty}(2j+1)e_q^{-\beta E_j} \approx \int_0^{\infty}(2j+1)e_q^{-\beta E(j)}\mathrm{d}j \\
&= \int_0^{\infty}(2j+1)[1-(1-q)hc\beta Bj(j+1)]^{\frac{1}{1-q}}\mathrm{d}j
\end{aligned}
$$

$$
= \frac{-1}{hc\beta B(2-q)}\left[[1-(1-q)hc\beta Bj(j+1)]^{\frac{2-q}{1-q}}\right]_0^{\infty} \tag{18}
$$

$$
= \frac{1}{hc\beta B(2-q)} = Z_{(2)}^{rot\,lin}\cdot\frac{1}{2-q}\ .
$$

In $\boxed{\text{the case } 1 < q < 2}$ the integral is solvable because $\lim_{j\to\infty}[1-(1-q)a\,j(j+1)]^{(2-q)/(1-q)} = 0$, because it is $(2-q)/(1-q) < 0$. In $\boxed{\text{the case } 0 < q < 1}$ we have again to cut the range of the integration. We only integrate to an upper border, such that $[1-(1-q)hcB\,j(j+1)]$ becomes zero. The same expression like in eq.(18) results. In both cases, we get the q-factor:

$$
A^{rot}(q,2) = \frac{1}{2-q} \text{ for } 0 < q < 2\ . \tag{19}
$$

For $q = 1$ we again get the classical formula. For an exact calculation by the Euler-Maclaurin formula, we get

$$
Z_{q(2)}^{rot} = \frac{1}{hc\beta B(2-q)} + \frac{1}{3} + \frac{hc\beta B}{15} + \frac{4(hc\beta B)^2}{315} + \cdots \tag{20}
$$

where the correction term with the q-part only emerges in the first summand. (It is also possible to include centrifugal distortion constants.[37]) If we generalize the factor to the formula for nonlinear molecules, we get

$$
Z_{q(3)}^{rot} = \sqrt{\pi}\left(\frac{1}{hc\beta B_1(2-q)}\right)^{1/2}\left(\frac{1}{hc\beta B_2(2-q)}\right)^{1/2}\left(\frac{1}{hc\beta B_3(2-q)}\right)^{1/2} \tag{21}
$$

$$
= Z_{(3)}^{rot}\left(\frac{1}{2-q}\right)^{\frac{3}{2}} \tag{22}
$$

and thus, the rotation-$q$-factor becomes

$$
A^{rot}(n,q) = \left(\frac{1}{2-q}\right)^{\frac{n}{2}} \text{ for } 0 < q < 2 \text{ and } n = 2,3. \tag{23}
$$

**Classical sum over vibrational states**

The vibrations of a molecule can be approximated by harmonic oszillators. A normal mode has the energy levels $E_i = (i+1/2)hc\nu$ with $i = 0,1,\cdots$. It gives the partition function

$$
Z_{(1)}^{vib} = \sum_{i=0}^{\infty}e^{-(i+1/2)hc\beta\nu} = \frac{e^{-hc\beta\nu/2}}{1-e^{-hc\beta\nu}} \tag{24}
$$

where $\nu$ is the frequency of the vibration. The energy levels are equidistant, and the sum is analytical. For a molecule, every degree of freedom adds this part to the sum over states.

$$Z_{(n)}^{vib} = Z_{(1)}^{vib}(\nu_1)\, Z_{(1)}^{vib}(\nu_2)\ldots Z_{(1)}^{vib}(\nu_n) = \prod_{j=1}^{n} \frac{e^{-hc\beta\nu_j/2}}{1 - e^{-hc\beta\nu_j}} = \frac{e^{-hc\beta\nu_0}}{\prod_{j=1}^{n}(1 - e^{hc\beta\nu_j})} \ . \tag{25}$$

The last equation uses the frequency of the zero point vibration $\nu_0 = \sum_j \nu_j/2$.

The approximation of the sum by an integration holds only under high temperatures if, say, $T > 10\frac{hc\nu}{k_B}$. In this case, we get the vibrational sum by

$$Z_{(1)}^{vib(ap)} \approx \frac{1}{hc\beta\nu} \ .$$

The result also holds if one approximates the exponential function in eq.(24) by $e^{-x} \approx 1-x$. For $n$ degrees of freedom we get

$$Z_{(n)}^{vib(ap)} = \prod_{j=1}^{n} Z_{(1)}^{vib(ap)}(j) \approx \prod_{j=1}^{n} \frac{1}{hc\beta\nu_j} = \frac{1}{(hc\beta)^n} \prod_{j=1}^{n} \frac{1}{\nu_j} \tag{26}$$

where $n = 3N - 6$ for a nonlinear, and $n = 3N - 5$ for a linear molecule.

**Approximation of a q-sum over vibrational states**

The formula for the generalized q-partition function for vibrations of a system with $n$ vibrational degrees of freedom is obtained in the approximation by $n$ harmonic oszillators, and in integral approximation (for high temperatures).[32] We use the Hamilton function $H(\mathbf{x}, \mathbf{p}) = \sum_{j=1}^{n}[\frac{1}{2m_j}p_j^2 + \frac{1}{2}m_j v_j^2 x_j^2]$, where it is $v_j = 2c\pi\nu_j$, and $m_j$ are the reduced masses. At the beginning, the range of integration is $x_j \in (-\infty, \infty)$ and $p_j \in (-\infty, \infty)$ for $j = 1 \ldots, n$. It is

$$Z_{q(n)}^{vib(ap)} = \frac{1}{h^n} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e_q^{-\beta H(x_1, \ldots, p_n)} dx_1 \ldots dp_n \ . \tag{27}$$

We get a 2n-dimensional q-integral

$$= \frac{1}{h^n} \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} \left(1 - (1-q)\left[\frac{\beta}{2m_j}\sum_{j}^{n} p_j^2 + \frac{m_j \beta c^2 \pi^2}{2}\sum_{j}^{n} \nu_j^2 x_j^2\right]\right)^{\frac{1}{1-q}} dx_1 \ldots dp_n \ . \tag{28}$$

The summands of the Hamiltonian are substituted by $y_j = \sqrt{\frac{m_j \beta}{2}}c\pi\nu_j x_j$ and $y_{n+j} = \sqrt{\frac{\beta}{2m_j}}p_j$, with $j = 1, \cdots, n$.

$$= \frac{1}{\prod_{j=1}^{n} \nu_j} \left(\frac{2}{hc\pi\beta}\right)^n \underbrace{\int_{0}^{\infty} \cdots \int_{0}^{\infty} \left(1 - (1-q)[y_1^2 + \ldots + y_{2n}^2]\right)^{\frac{1}{1-q}} dy_1 \ldots dy_{2n}}_{q-\text{integral in appendix with 2n}} \ . \tag{29}$$

12

Thus

$$
Z_{q(n)}^{vib(ap)} = \frac{1}{(hc\beta)^n \prod_{j=1}^{n} \nu_j} \cdot
\begin{cases}
\dfrac{1}{(q-1)^n} \dfrac{\Gamma(\dfrac{1}{q-1} - n)}{\Gamma(\dfrac{1}{q-1})} & \text{for } 1 < q < 1 + \frac{1}{n} \\[4ex]
\dfrac{1}{(1-q)^n} \dfrac{\Gamma(\dfrac{1}{1-q} + 1)}{\Gamma(\dfrac{1}{1-q} + n + 1)} & \text{for } 0 < q < 1 \ .
\end{cases}
\tag{30}
$$

Because the $n$-arguments of the Gamma functions are integers, the corresponding factors are to be reduced by the relation $\Gamma(y) = (y-1)\Gamma(y-1)$. It results (cf. ref. [38] for $0 < q < 1$, and ref. [32] for $1 < q$)

$$
Z_{q(n)}^{vib(ap)} = \frac{1}{(hc\beta)^n} \prod_{j=1}^{n} \frac{1}{\nu_j} \frac{1}{j+1-jq} = \frac{1}{(hc\beta)^n} \prod_{j=1}^{n} \frac{1}{\nu_j} \cdot A^{vib}(n, q) \ ,
\tag{31}
$$

and the q-factor for the vibrations in $\boxed{\text{both cases } 0 < q < 1 \text{ or } 1 < q}$ is

$$
A^{vib}(n, q) = \prod_{j=1}^{n} \frac{1}{j+1-jq} \ .
\tag{32}
$$

The factor remains greater than zero for $0 < q < 1 + \frac{1}{n}$. Again, here the $\lim_{q \to 1} Z_q$ coincides with the classical partition function for $n$ harmonic oszillators in this approximation for high temperatures. To get an exact description of the sum of vibrational states by the Tsallis statistics, one has to go back to the sum

$$
Z_{q(1)}^{vib} = \sum_{i=0}^{\infty} (1 - (1-q)(i+1/2)hc\beta\nu)^{\frac{1}{1-q}} \ .
\tag{33}
$$

It is not analytically calculable, however, numerically it is. Again, the sum is to cut if the term $(1 - (1-q)(i+1/2)hc\beta\nu)$ becomes less than zero, in the case $q < 1$.

### Electronic part

Electronic energies of molecules are very large, in comparison to temperature. Thus, $e^{-\beta E_j}$ becomes very small for small $j$ yet. If we put the zero point of the energy scale to the electronic energy of the ground state, then only the degree of degeneration of the ground state enforces an additional value, $g_1$.

$$
Z^{el} = \sum_{i=1}^{\infty} g_i e^{-\beta E_j} \approx g_1
\tag{34}
$$

where $g_1$ is one, in most cases. Thus, the electronic part does not play any role here.

**q-generalized partition functions**

We summarize all results in the q-generalized sum over states

$$Z_q^{mol} = Z_{q(n_{trans})}^{trans} \, Z_{q(n_{rot})}^{rot} \, Z_{q(n_{vib})}^{vib} \, Z^{el} \,. \tag{35}$$

In this expression couplings between the electronic, vibrational, and rotational degrees of freedom are neglected. The translational degrees of freedom are $n_{trans} = 3$. If the molecule has $N$ atoms, and if it is linear, then $n_{rot} = 2$, and $n_{vib} = 3N - 5$. If it is nonlinear, then it is $n_{rot} = 3$, and $n_{vib} = 3N - 6$. At all it holds $n_{trans} + n_{rot} + n_{vib} = 3N$. We get

$$Z_q^{mol} = Z^{mol} \cdot A(3N, q) \tag{36}$$

and the q-factor is composed by $A^{trans}(3, q)$ with eq.(11), by $A^{rot}(n_{rot}, q)$ with eq.(23), and $A^{vib}(n_{vib}, q)$ with eq.(32):

$$A(3N, q) = \left(\frac{1}{2-q}\right)^{n_{rot}/2} \prod_{j=1}^{n_{vib}} \frac{1}{1+j-qj} \cdot \begin{cases} \dfrac{1}{(q-1)^{\frac{3}{2}}} \dfrac{\Gamma(\dfrac{1}{q-1} - \dfrac{3}{2})}{\Gamma(\dfrac{1}{q-1})} & \text{for } 1 < q \\[4mm] \dfrac{1}{(1-q)^{\frac{3}{2}}} \dfrac{\Gamma(\dfrac{1}{1-q} + 1)}{\Gamma(\dfrac{1}{1-q} + \dfrac{5}{2})} & \text{for } 0 < q < 1 \,. \end{cases} \tag{37}$$

In the upper case, the $q$-value is restricted by the vibrational dimension to $q < 1 + \frac{1}{n_{vib}}$ (as well as in the translational part to $q < 1 + \frac{2}{3}$, and in the rotational part to $q < 2$). Larger values of $q$ do not form any useful physical model of a distribution.

## Arrhenius equation and Transition State Theory

The Arrhenius equation[7] is for the reaction velocity $k$

$$k(T) = A e^{-\Delta E/RT} \,. \tag{38}$$

The prefactor $A$ and the activation energy $\Delta E$ are to be determined by experiment. In logarithmic form, $\ln k = \ln A - \Delta E/RT$, the equation is often used for a linear graphical representation of $\ln k$ against $1/T$. The factor $e^{-\Delta E/RT}$ is interpreted to be the probability, that a particle under a collision by temperature $T$ has the energy $\Delta E$ (Boltzmann distribution). It works well for $\Delta E \gg RT$.

**The Eyring equation of the Transition State Theory**

The idea of the TS is the extra part of the degree of vibration which goes along the pass-valley

$$Z^{vib}(\nu) = \frac{1}{(1 - e^{\frac{-h\nu}{k_B T}})} \approx \frac{k_B T}{h\nu} \ . \tag{39}$$

This part is to be separated from the remainder of the partition function. The well known Eyring equation then becomes[1,2,3]

$$k^{TST} = \frac{k_B T}{h} \frac{Z_{TS}}{(N_A V)^{\Delta\gamma} Z_R} e^{-\frac{\Delta E}{k_B T}} \ , \tag{40}$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature, $h$ is the Planck constant, $N_A$ is the number of particles, $V$ is the volume, $\Delta\gamma$ is the change of the stoechiometric relation of the reaction, $Z_{TS}$ is the partition function of the TS, and $Z_R$ is the partition function of the reactant. The energy difference between R and TS is $\Delta E$.

If we try to generalize the Eyring equation for an assumed Tsallis statistics at the TS, and if we accept all the approximations made in the last sections, then we obtain a simple factorization of $k_q^{TST}$. Without bias, such a relation is by no means trivial. We still have to reduce the q-factor for $(n_{vib} - 1)$ vibrational states across the TS valley. As aforementioned, we propose the ansatz
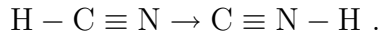
$$k_q^{TST} = A(3N - 1, q) \cdot k^{TST} \tag{41}$$

where

$$A(3N - 1, q) = A^{trans}(3, q) \ A^{rot}(n_{rot}, q) \ A^{vib}(n_{vib} - 1, q) \ . \tag{42}$$

## Example: HCN

The first example is the isomerization of the molecule hydrogen cyanide

$$H - C \equiv N \rightarrow C \equiv N - H \ .$$

The system has 3 atoms: it is really small by molecular standards. The reaction is the prototype of an isomerization with a metastable state. The linear HCN molecule has three vibrational states, one bending mode $\nu_2$, with $\nu_2 = 1$ being $\approx$1000 K above the ground state, and two stretching vibrations: $\nu_1$, corresponding to the CN stretch, where $\nu_1 = 1$ is $\approx$3000 K above the ground state, and $\nu_3$, the CH stretch, with $\nu_3 = 1$ being $\approx$4700 K above

the ground state.[39] Thus, the bond energies are greatly in excess of $\beta^{-1} = k_B T$, and we may use the rigid rotator - harmonic oscillator ansatz for HCN. The bending mode $\nu_2$ is doubly degenerate; for $\nu_2 \neq 0$ this degeneracy is lifted and the levels are split by rotation-vibration interaction. A new quantum number $l$ (where $l = \nu, \nu - 2, ..., -\nu$) is needed to describe the system. Overtones and combination bands exist as well. The geometry of reactant HCN, and of the TS is given in Table I and Table II.[40]

The Eyring equation (40) for the reaction is

$$k_{TST}^{HCN}(T) = \frac{k_B T}{h}(N_A V)^0 \frac{Z_{TS}}{Z_{HCN}} e^{-\frac{\Delta E}{k_B T}} = \frac{k_B T}{h} \underbrace{\frac{Z_{TS}^{trans}}{Z_{HCN}^{trans}}}_{1} \frac{Z_{TS}^{rot}}{Z_{HCN}^{rot}} \frac{Z_{TS}^{vib}}{Z_{HCN}^{vib}} \underbrace{\frac{Z_{TS}^{el}}{Z_{HCN}^{el}}}_{1} e^{-\frac{\Delta E}{k_B T}} . \quad (43)$$
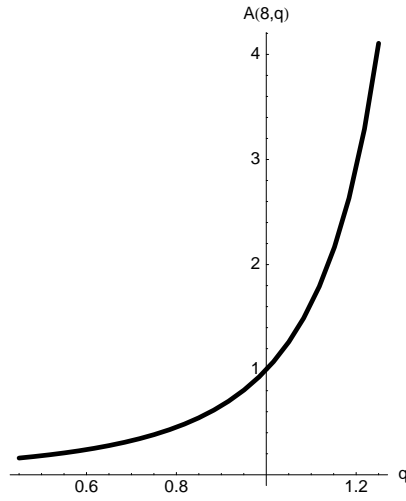


**FIGURE 2**. Tsallis factor $A^{uni}(8,q)$ with eq.(44) for a triatomic molecule.

The quotient of the electronic sum does not change over the reaction. In case of a unimolecular reaction, the $Z^{trans}$ is also the same for R and TS. If we assume a Tsallis distribution for vibrational and rotational states at the TS, then the $q$-factor for the Eyring equation,

Table I. HCN Jacobi coordinates; $s$, $r$ in Å, $\theta$ in °

|  | reactant | TS |
|---|---|---|
| $s$ | 1.155 | 1.186 |
| $r$ | 1.685 7 | 1.155 |
| $\theta$ | 0.0 | 76.42 |

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**Table II**. HCN: Cartesian coordinates in Å

|   | reactant | | | TS | | |
|---|---|---|---|---|---|---|
|   | H | C | N | H | C | N |
| $x$ | 1.109 3 | 0.0 | 1.155 | 0.321 7 | 0.0 | 0.864 |
| $y$ | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| $z$ | 0.0 | 0.0 | 0.0 | 1.122 8 | 0.0 | 0.0 |

$A(3N-1, q)$, is with eq.(42)

$$A^{uni}(8, q) = A^{rot}(3, q) \cdot A^{vib}(2, q)$$

$$= \left(\frac{1}{2-q}\right)^{\frac{5}{2}} \cdot \frac{1}{3-2q} \tag{44}$$

The vibrational part is a valid model if $q < 3/2$. (If one would additionally include the q-translational factor, one would get a steeper curve, near 1: the values are still smaller for $q < 1$, but even larger for $q > 1$.)   A piece of the $q$-factor $A^{uni}(8, q)$ for triatomic molecules is shown in Fig.2. In Table III we present some of the $q$-factors. Even for small variations of $q$ important factors result.

**Table III**. Tsallis $q$-factors for triatomic molecules

| $q > 1$ | $A^{uni}(8, q)$ | $q < 1$ | $A^{uni}(8, q)$ |
|---|---|---|---|
| 1.000 1 | 1.000 4 | 0.999 9 | 0.999 6 |
| 1.001 | 1.004 5 | 0.999 | 0.995 5 |
| 1.005 | 1.022 8 | 0.995 | 0.977 8 |
| 1.01 | 1.046 4 | 0.99 | 0.956 3 |
| 1.05 | 1.263 1 | 0.95 | 0.804 7 |
| 1.1 | 1.626 7 | 0.9 | 0.656 7 |
| 1.15 | 2.144 6 | 0.85 | 0.542 4 |
| 1.2 | 2.911 6 | 0.8 | 0.452 8 |
| 1.25 | 4.105 6 | 0.75 | 0.381 6 |
| 1.3 | 6.089 1 | 0.7 | 0.324 4 |
| 1.35 | 9.785 8 | 0.6 | 0.239 6 |
| 1.4 | 17.930 5 | 0.5 | 0.181 4 |
| 1.45 | 44.575 2 | 0.4 | 0.140 4 |

To calculate the rotational partition functions, we use the masses in $g/mol$ $m_H = 1.008$, $m_C = 12.011$, and $m_N = 14.007$; the molecular mass is 27.026. The rotational constants of HCN, and of the TS are obtained by the moments of the molecule. It is[29]

$$B^{HCN} = 1.466\,18\,cm^{-1}\ ,$$

$$B_1^{TS} = 13.94946\,cm^{-1}, \qquad B_2^{TS} = 1.618\,68\,cm^{-1}, \qquad B_3^{TS} = 1.831\,16\,cm^{-1}\ .$$

The rotational partition functions are at any temperature (in $K$) with eqs.(14) and (17)

$$Z_{HCN}^{rot} = \frac{1}{hc\beta B^{HCN}} = 0.474 \cdot T\ ,$$

$$Z_{TS}^{rot} = \frac{\sqrt{\pi}}{\sqrt{h^3 c^3 \beta^3 B_1^{TS} B_2^{TS} B_3^{TS}}} = 0.159\,72 \cdot \sqrt{T^3}\ .$$

For the sum over vibrational states we use the normal modes and formula (24). This approximation is useful. We use the PT2-frequencies of ref.[41] in Table IV. The data coincide with those of ref.[40] and experimental data.

**Table IV**. HCN vibrational frequencies (in $cm^{-1}$)

| reactant | | TS | |
| --- | --- | --- | --- |
| $\nu_1^{HCN}$ | 2\,097.26 | $\nu_1^{TS}$ | 2\,157.66 |
| $\nu_2^{HCN}$ | 715.41 | | |
| $\nu_3^{HCN}$ | 3\,308.67 | $\nu_3^{TS}$ | 3\,002.08 |
| $\nu_0^{HCN}$ | 3\,480.83 | $\nu_0^{TS}$ | 2\,647.60 |

The frequency of the zero point vibration is only composed by two parts in the case of the TS: the "bending vibration" over the TS is no state of the TS. It is the direction of the reaction. With formula (24) we get the vibrational partition functions for $T$ (in $K$)

$$Z_{HCN}^{vib} = \frac{e^{-\frac{hc\nu_0}{k_B T}}}{(1-e^{-\frac{hc\nu_1}{k_B T}})(1-e^{-\frac{hc\nu_2}{k_B T}})^2(1-e^{-\frac{hc\nu_3}{k_B T}})}$$

$$= \frac{e^{-5\,008.132/T}}{\left(1-e^{-3\,017.486/T}\right)\left(1-e^{-1\,029.314/T}\right)^2\left(1-e^{-4\,760.433/T}\right)}\ ,$$

$$Z_{TS}^{vib} = \frac{e^{-\frac{hc\nu_0}{k_B T}}}{(1-e^{-\frac{hc\nu_1}{k_B T}})(1-e^{-\frac{hc\nu_3}{k_B T}})} = \frac{e^{-3\,809.302/T}}{\left(1-e^{-3\,104.388/T}\right)\left(1-e^{-4\,319.319/T}\right)}\ .$$

Table V reports the partition functions of the HCN molecule and of the TS at various temperatures, which coincide with some special values in refs.[42] Even though the calculation uses the harmonic oscillator approximation, the deviations for HCN vibrations are very small against the exact calculated sum over states, which are obtained by the sum of "all" known energy levels of the HCN.[43] We use the $\Delta E = 0.334\,601 \cdot 10^{-18}\,J$ for the TS of HCN, or transformed into wavenumbers $16\,844\,cm^{-1}$, or $48.12\,kcal/mol$, for the height

of the energy barrier.[44,45] The last column in Table VI contains the figures of the Eyring equation of the reaction rate $k_{TST}$. (Note that the rates coincide with results of variational TST calculations for HCN,[46] if the corresponding, older barrier height is used.)

**Application:** To our best knowledge, we could not find any experimental rate of the HCN isomerization. The existence of the HCN to HNC isomerization reaction was clearly seen by Maki and Sams[47] in 1981, cf. also the recent experiments of Mellau et al.[48] The infrared measurements of these workers used heated cells over some hours, and they could not give hints to the exact reaction rate. There is an experimental comparison of a theoretical reaction rate $k_{Lin}$.[49] It is an indirect conclusion. There is a article[50] with some mild questions about the figure $k_{Lin}$, but these authors could not give any other appraisal. Nevertheless, $k_{Lin}$ is used in the JANAF table[51] for the HCN reaction rate.

In this work here, we try to adapt the theoretical reaction rate to an experimental one by a parameter, the Tsallis $q$-value. At $T = 700\,K$ Lin et al. work with $k_{Lin} = 6.0 \cdot 10^{-2} s^{-1}$. The value is used to explain the further use up of the reaction product, HNC, in a following reaction. If we compare the value with the $k_{TST}$ from Table V, we could adapt that value to the Lin-value by a Tsallis factor of $A^{uni}(8, q) = 0.1525$. It corresponds to $q = 0.433$ (see Table III). By the $q$ we could reproduce the quasi-experimental result. However, we note that the $k_{Lin}$ is based on an obsolete, older PES (by Murell et al.[52]). Lin et al. remarked that an experimental value is needed. The large difference between our $k_{TST}$ and the $k_{Lin}$ challenges to a check of the experimental data.

**Table V**. Rotational and vibrational sums of HCN at different temperatures

| $T$ (in K) | $Z_{HCN}^{vib}$ | $Z_{TS}^{vib}$ | $Z_{HCN}^{rot}$ | $Z_{TS}^{rot}$ |
|---|---|---|---|---|
| 298 | $5.361 \cdot 10^{-8}$ | $2.808 \cdot 10^{-6}$ | 141.265 | 821.647 |
| 400 | $4.282 \cdot 10^{-6}$ | $7.316 \cdot 10^{-5}$ | 189.618 | 1277.765 |
| 500 | $5.884 \cdot 10^{-5}$ | $4.923 \cdot 10^{-4}$ | 237.022 | 1785.731 |
| 700 | $1.337 \cdot 10^{-3}$ | $4.393 \cdot 10^{-3}$ | 331.831 | 2958.068 |
| 1000 | $1.716 \cdot 10^{-2}$ | $2.352 \cdot 10^{-2}$ | 474.044 | 5050.811 |
| 1500 | $1.734 \cdot 10^{-1}$ | $9.568 \cdot 10^{-2}$ | 711.066 | 9278.932 |
| 2000 | $7.147 \cdot 10^{-1}$ | $2.135 \cdot 10^{-1}$ | 948.089 | 14258.851 |

**Table VI**. Factors of the Eyring equation

| $T$ (in K) | $\frac{k_B T}{h}$ | $\frac{Z_{TS}^{rot}}{Z_{HCN}^{rot}} \cdot \frac{Z_{TS}^{vib}}{Z_{HCN}^{vib}}$ | $e^{-\frac{\Delta E}{k_B T}}$ | $k_{TST}$ [s$^{-1}$] |
|---|---|---|---|---|
| 298 | $6.209 \cdot 10^{12}$ | 304.701 | $4.794 \cdot 10^{-36}$ | $9.071 \cdot 10^{-21}$ |
| 400 | $8.335 \cdot 10^{12}$ | 115.139 | $4.866 \cdot 10^{-27}$ | $4.670 \cdot 10^{-12}$ |
| 500 | $1.042 \cdot 10^{13}$ | 63.038 | $8.907 \cdot 10^{-22}$ | $5.850 \cdot 10^{-7}$ |
| 700 | $1.459 \cdot 10^{13}$ | 29.295 | $9.206 \cdot 10^{-16}$ | $3.935 \cdot 10^{-1}$ |
| 1 000 | $2.083 \cdot 10^{13}$ | 14.605 | $2.984 \cdot 10^{-11}$ | $9.079 \cdot 10^{3}$ |
| 1 500 | $3.125 \cdot 10^{13}$ | 7.200 | $9.621 \cdot 10^{-8}$ | $2.165 \cdot 10^{7}$ |
| 2 000 | $4.167 \cdot 10^{13}$ | 4.501 | $5.463 \cdot 10^{-6}$ | $1.025 \cdot 10^{9}$ |

## Example: $H_2 + CN \rightarrow H + HCN$

The kinetics of cyano species (CN,HCN) are of interest in modeling combustion of fuels. The example reaction is a diatom-diatom reaction. The pseudo-halogen character of the CN radical causes that the reaction with $H_2$ proceeds through a hydrogen abstraction to form HCN, with $\Delta H_{298}^0 = -69\,\mathrm{kJ\,mol^{-1}}$.[53] The TS of the reaction is linear.[54] At the TS, we have 12 degrees of freedom: 3 translational, 2 rotational, and 7 vibrational degrees. But only 6 vibrational modes cut across the TS. Thus it is

$$A(11, q) = A^{trans}(3, q) \ A^{rot}(2, q) \ A^{vib}(6, q), \qquad (45)$$

using the formulas (11), (23), and (32). The $q$-factor $A(11, q)$ for a 4-atomic, linear system,
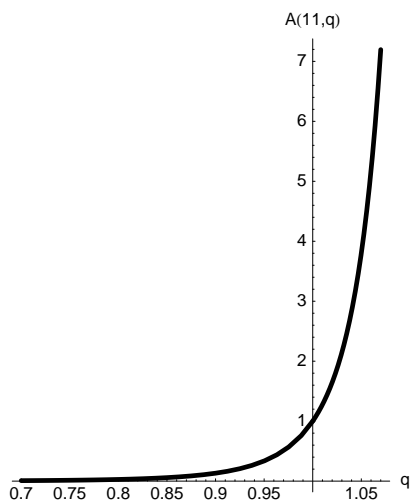


**FIGURE 3**. Tsallis factor A(11,q) with eq.(45) for a linear 4-atomic molecule.

like the TS of the reaction in question, is exhibited in Fig.3. Already for very small variations of $q$ important factors result. $q$ is restricted by $A^{vib}(6, q)$ to $q < 1 + 1/6 = 1.1\overline{6}$.

The rate coefficients for the reaction exhibit a pronounced temperature dependence. The Arrhenius plot (Fig. 4) shows a set of three measurements: data by Sun et al.,[55] Sims and Smith,[56] and Atakan et al.[53] The Sun data are the highest, these of Atakan are the lower one, and those of Sims and Smith are nearer to the Sun data, but something in between to the Atakan data. The Fig. 4 makes the results of our investigation of a q-factor for the
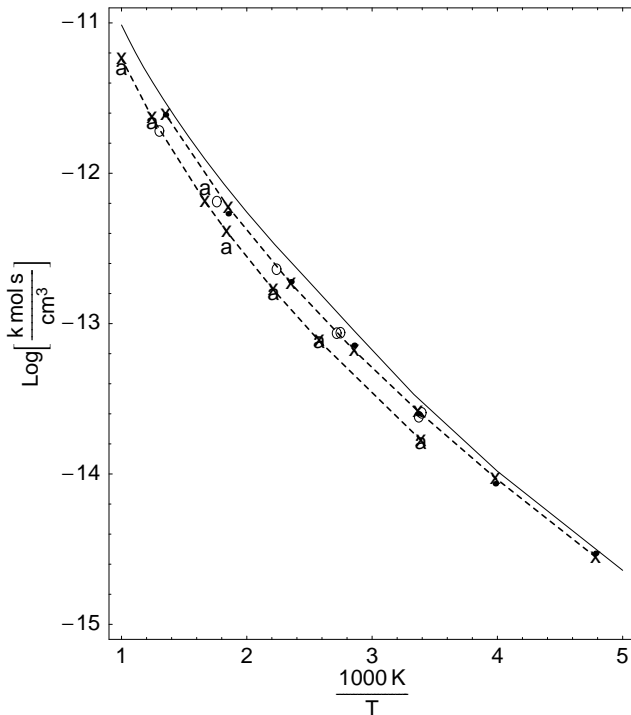


**FIGURE 4**. Arrhenius plot of the rate of $H_2+CN \rightarrow H+HCN$. Experimental data of Sun et al.[55] ($\bullet$), of Sims and Smith[56] (o), and of Atakan et al.[53] (**a**). The full line corresponds to a variational TST calculation.[55] It is readjusted to two sets of data by Tsallis q-factors 0.99555, and 0.9777, correspondingly, for the upper and the lower dashed curve. The crosses (**x**) are the values moved from the VTST curve for comparison.

4-atomic reaction vividly imaginable. We use a variational TST result of Sun et al.[55] for comparison. Note, there is a similar result of a conventional TST calculation[57] (with Wigner tunneling), as well as a result of an improved canonical variational TST calculation.[58] (The latter is larger than the rates calculated by scattering theory. – It cannot be overstressed that a scattering theory based expression is correct.[59]) If we choose $q = 0.9955$, we can adapt the calculated curve to the measured values of Sun et al.[55] However, if we choose $q = 0.9777$ then it fits very well the calculated curve with the measured values of Atakan et

al.[53], see Fig. 4. The accordance of the slopes of two series of data with the TST calculation – corrected by a Tsallis factor – seems fine. The difference of the two curves indicates that one of them may have a systematic scaling problem. However, the skew slope of the Sims and Smith data[56] could indicate that they are not correct.

## Discussion

Various approximations are used for the q-partition functions treated in this article. First, the factorization of $Z$ into $Z_{trans}$, $Z_{rot}$, and $Z_{vib}$. Second, like in the classical TST, we also used some approximations of sums by integrals, and, of course, the harmonic oscillator - rigid rotator ansatz. We assume that the diverse approximations do not disturb the important difference of the distributions which are open for discussion: Boltzmann, or its extension, Tsallis distribution. The last one, the distribution for non-equilibrium processes, opens a nice way to adapt measured rates to a theoretical rate given by any TST. This article can only be a first step on the way. The two examples used show the advantages of the idea. It is clear that the higher $n_{vib}$ in eq.(42) is, the nearer to one we may choose the q-factor to amend TST calculations to reproduce the experimental results. The factor $A^{vib}$ in eq.(42) is the most important part of the formula of $A(3N - 1, q)$, as well as the strongest. The other parts can be called into question. In unimolecular transitions, like in HCN isomerization, we do not use the extra part $A^{trans}$ at all, because the center of mass of a molecule behaves equally at reactant and TS. Like that, one may also restrict the use of $A^{rot}$. Because, in contrast to vibrational transitions, strong selection rules govern the rotational transitions: only $\Delta j = 0, \pm 1$ is possible, other transitions are forbidden. There are only P-, Q-, and R-branch lines in the infrared spectrum.[60] See ref.[61] for a nice example in HCN. A quick redistribution of rotational states could be impossible, on the pathway from reactant to TS. Thus, one could also assume that one and the same distribution governs the rotational states at reactant and at TS. However, at least for vibrational states we propose the Tsallis distribution at TS.

We note that another q-variant of the Arrhenius equation for the rate constant of a chemical

reaction has recently been presented[32,62,63]

$$k_q = A \frac{\exp_q(-E^\#/k_B T)}{\exp_q(-E_0/k_B T)} \tag{46}$$

where $A$ is again a pre-q-exponential factor, $E^\#$ is the energy of the transition state and $E_0$ is that of the ground state, the reactant. As $q \approx 1$, $k_q$ approaches the Arrhenius form $k = A \exp(-\Delta E/k_B T)$, where $\Delta E = E^\# - E_0$ is the activation energy. Formula (46) is used in enhanced sampling methods. In contrast, our ansatz in this article proposes the Tsallis distribution at the TS only: we assume the validity of the Boltzmann-Gibbs distribution at the minimum. The Tsallis distribution is then behind the pre-q-exponential factor.

We remark that the proposed Tsallis distribution at the TS does not jeopardize the different changes of TST by versions of a variational TST.[59] It is a matter of fact that a "stable occupation" of vibrational or rotational levels "across to the TS" can change the geometry of the TS (and, of course, it rises the absolute height of the barrier). For example HCN, a calculation[64] results in a movement of the TS by $2^o$ along the TS valley, if the rotational levels increase from $j = 0$ to $j = 70$. Thus, the "ground"-TS, the col of the PES where no further states are occupied, is only the calculable point in configuration space which we use for the classical TST. Approximations which move the TS are independent on the treatment of the distribution of states at the TS.

This remark also applies to diverse theories of tunneling through the barrier.


There still emerges a side problem. We feel here the necessity to discuss the "rate", the relation of the number of results in theory and experiment. There are dozens of theoretical papers discussing the HCN isomerization; however, there does not exist one experimental reaction rate. Nearly every new ansatz in theoretical chemistry has been applied to HCN, over the last years, and compared, of course, with older reaction rates. However, by missing any experiment, the comparison restricts to older theoretical values.

On the other hand, the molecule HCN is one of the best known molecules, from the point of view of infrared spectroscopy. Probably there are the most states assigned, at all, see Mellau et al.[48] and references therein, and ref.[65] However, experimental values of the reaction rate for the isomerization to HNC are open. We challenge the experimental groups of the world to deliver this value. There is a deep need to measure these reaction rates, to give severe

values for a plethora of theories.[66] Further experiments are crucial.

## Conclusion

A special parameter, $q$, of a Tsallis distribution of the probabilities of states at the pass of the reaction $H_2 + CN \rightarrow H + HCN$ could adapt a TST result to the known experimental rate. However, this intriguing example goes on by another distribution than the long treated Boltzmann-Gibbs distribution. A "near-Boltzmann" approximation was discussed only sporadically in the past,[67] but without proposing the Tsallis distribution. Tsallis weight factors, instead of Boltzmann probability weight factors, are used for the method of stimulated annealing.[32,68] Examples of enhanced sampling with Tsallis are done.[69] However, also the Tsallis weight factors are not applied to TST, up to date. We propose to use the Tsallis factor, eq.(42), to extend the traditional TST.

Why a Tsallis distribution at TS may better explain a rate experiment, than a Boltzmann distribution, and which $q$ is to choose in any current case, is open for further research. Of course, there is a need to test the parameter $q$ in various reactions for series of molecules.

## Appendix: the n-dimensional $q$-integral

The integral emerges in the calculation of the q-partition functions for the Tsallis distribution. It is

$$I = \int_0^\infty \ldots \int_0^\infty \left(1 - (1-q)[y_1^2 + \ldots + y_n^2]\right)^{\frac{1}{1-q}} \mathrm{d}y_1 \ldots \mathrm{d}y_n \ .$$

Coordinates transformation to $n$-dimensional hyperspherical coordinates results in

$$I = \int_0^\infty [1 - (1-q)\, r^2]^{\frac{1}{1-q}} r^{n-1} \mathrm{d}r \prod_{j=1}^{n-1} \int_0^{\pi/2} \cos^{j-1} \varphi_j \mathrm{d}\varphi_j \ .$$

The radial part goes on with some transformations: first, for $\boxed{\text{the case } 1 < q}$, the substitution $[1 - (1-q)r^2] = \frac{1}{1-t}$ is used, it moves the integration from $(0; \infty)$ to $(0; 1)$ and it is $dr = \mathrm{d}t/2\sqrt{q-1}(1-t)^{3/2}t^{1/2}$. We use the properties of the Gamma integral $\int_0^1 x^a (1-x)^b dx = \dfrac{\Gamma(a+1)\Gamma(b+1)}{\Gamma(a+b+2)}$ (for $a$, $b > -1$), and $\Gamma(\frac{1}{2}) = \sqrt{\pi}$. Then[70]

$$\int_0^\infty [1-(1-q)\,r^2]^{\frac{1}{1-q}} r^{n-1}\mathrm{d}r \;=\; \frac{1}{2(q-1)^{n/2}} \int_0^1 (1-t)^{(\frac{1}{q-1}-\frac{n}{2}-1)}\, t^{(\frac{n}{2}-1)}\mathrm{d}t$$

$$= \tfrac{1}{2}\,\frac{1}{(q-1)^{n/2}}\, \frac{\Gamma(\dfrac{1}{q-1}-\dfrac{1}{2})\,\Gamma(\dfrac{n}{2})}{\Gamma(\dfrac{1}{q-1})}\;.$$

(47)

We obtain a restriction $q < 1 + 2/n$. It derives from the range of the existence of the $\Gamma$-integral at $t \to 1$.

$\boxed{\text{The case } 0 < q < 1}$ analogously develops with a somewhat modified substitution. We use here $[1-(1-q)r^2]=t$, $r=\sqrt{\dfrac{1-t}{1-q}}$ with the range of integration being again $(0,1)$; however, we only count values for $r$ where the integrand is not less than zero. The former upper border for $r$, $\infty$, is not exhausted here; however, the integration has to run up to $\sqrt{\frac{1}{1-q}}$. That forms the new range $(0,1)$ for $t$. For higher $r$-values the term $[1-(1-q)r^2]$ would be negative. There the integration is cut: the distribution presents a cut-off. For $q$ values near one, the possible error of the approximation is small. It is $\mathrm{d}r = \dfrac{-\mathrm{d}t}{2\sqrt{(1-q)(1-t)}}$, and we get

$$\int_0^{\sqrt{1/(1-q)}} (1-(1-q)y^2)^{\frac{1}{1-q}}\; r^{n-1}\mathrm{d}y$$

(48)

$$= \tfrac{1}{2}\frac{1}{(1-q)^{n/2}} \int_0^1 t^{\frac{1}{1-q}}(1-t)^{(\frac{n}{2}-1)}\mathrm{d}t = \tfrac{1}{2}\frac{1}{(1-q)^{n/2}} \frac{\Gamma(\frac{1}{1-q}+1)\,\Gamma(\frac{n}{2})}{\Gamma(\frac{1}{1-q}+\frac{n}{2}+1)}\;.$$

All in all, we get

$$I \;=\; \tfrac{1}{2}\Gamma(\tfrac{n}{2})\prod_{j=1}^{n-1}\int_0^{\pi/2}\cos^{j-1}\varphi_j \mathrm{d}\varphi_j \cdot \begin{cases} \dfrac{1}{(q-1)^{\frac{n}{2}}}\dfrac{\Gamma(\frac{1}{q-1}-\frac{n}{2})}{\Gamma(\frac{1}{q-1})} & \text{for } 1<q<1+\tfrac{2}{n} \\[3mm] \dfrac{1}{(1-q)^{\frac{n}{2}}}\dfrac{\Gamma(\frac{1}{1-q}+1)}{\Gamma(\frac{1}{1-q}+\frac{n}{2}+1)} & \text{for } 0<q<1\;. \end{cases}$$

The part of the angles is by recursion

$$\prod_{j=1}^{n-1}\int_0^{\pi/2}\cos^{j-1}\varphi_j \mathrm{d}\varphi_j = \begin{cases} \dfrac{1}{(n-2)(n-4)\ldots 4\,2}\,(\pi/2)^{n/2} & \text{if } n \quad\text{even} \\[4mm] \dfrac{1}{(n-2)(n-4)\ldots 5\,3}\,(\pi/2)^{(n-1)/2} & \text{if } n \quad\text{odd}\;. \end{cases}$$

We get

$$I \;=\; \left(\frac{\sqrt{\pi}}{2}\right)^n \cdot \begin{cases} \dfrac{\Gamma(\frac{1}{q-1}-\frac{n}{2})}{(q-1)^{\frac{n}{2}}\Gamma(\frac{1}{q-1})} & \text{for } 1<q<1+\tfrac{2}{n} \\[5mm] \dfrac{\Gamma(\frac{1}{1-q}+1)}{(1-q)^{\frac{n}{2}}\Gamma(\frac{1}{1-q}+\frac{n}{2}+1)} & \text{for } 0<q<1\;. \end{cases}$$

## Acknowledgments

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