



The rate coefficients of unimolecular reactions in the systems with power-law distributions



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HIGHLIGHTS

- The rate coefficient formulae of unimolecular reactions are generalized to systems with power-law distributions.
- The power-law rate coefficients are derived for unimolecular reactions in both the high and low pressure limits.
- The new rate coefficients are exactly in agreement with the measurements in experimental studies.

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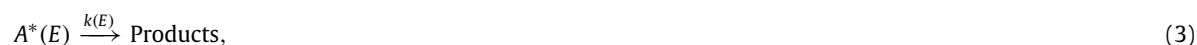
ABSTRACT

The rate coefficient formulae of unimolecular reactions are generalized to the systems with the power-law distributions based on nonextensive statistics, and the power-law rate coefficients are derived in the high and low pressure limits, respectively. The numerical analyses are made of the rate coefficients as functions of the ν -parameter, the threshold energy, the temperature and the number of degrees of freedom. We show that the new rate coefficients depend strongly on the ν -parameter different from one (thus from a Boltzmann–Gibbs distribution). Two unimolecular reactions, $\text{CH}_3\text{CO} \rightarrow \text{CH}_3 + \text{CO}$ and $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$, are taken as application examples to calculate their power-law rate coefficients, which obtained with the ν -parameters slightly different from one can be exactly in agreement with all the experimental studies on these two reactions in the given temperature ranges.

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1. Introduction

Unimolecular reactions are in principle the simplest type of chemical reactions that can occur in the gas phase since the reactions formally involve only one molecule. The theory of unimolecular reactions in the gas phase is a classical topic in physical chemistry [1]. When a molecule is supplied with an amount of energy that exceeds some threshold energy, the unimolecular reaction can take place, that is, dissociation or isomerization. In more advanced treatments of the unimolecular reactions, the mechanism, in the general case of the presence of a foreign gas, has the following scheme [2]:



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where M is an (inert) buffer gas, or any molecule that does not react with the molecule A , which could be A itself. A^* is a highly vibrationally excited molecule A . A^* is created in an activation step in reaction (1), which is a thermal activation, due to inelastic collisions, where translational energy is converted to vibrational energy. $dk_1(E)$ is the rate coefficient for activation of the molecule to an energy of the range $[E, E + dE]$. Reaction (2) means that A^* can be de-energized with a rate coefficient k_{-1} . Note that k_{-1} is assumed to be independent of the energy. After (or during) the creation of A^* , intramolecular vibrational energy redistribution (IVR) will take place, and thus the vibrational energy will redistribute and spread to all vibrational degrees of freedom in the molecule. In reaction (3), the reaction rate coefficient $k(E)$ is assumed a constant reaction probability per unit time at the internal energy E . For the activated molecule, the dynamical equation is

$$\frac{dA^*(E)}{dt} = dk_1(E) [A] [M] - k_{-1} [A^*(E)] [M] - k(E) [A^*(E)], \quad (4)$$

where $[\dots]$ denotes the concentration. There exists a steady state approximation, and then we have

$$A^*(E) = \frac{dk_1(E) [A] [M]}{k_{-1} [M] + k(E)}. \quad (5)$$

The rate of the reaction is

$$\nu = k(E) A^*(E) = \frac{k(E) dk_1(E) [A] [M]}{k_{-1} [M] + k(E)}. \quad (6)$$

Note that the rate, in general, is a function of $[M]$.

In the high pressure limit, the rate is given by a first order expression in $[A]$, and thus from Eq. (6) we have the unimolecular reaction rate coefficient at the energy E [2],

$$k_{\text{uni}}^\infty(E) = \lim_{[M] \rightarrow \infty} \frac{\nu}{[A]} = \frac{k(E) dk_1(E)}{k_{-1}}. \quad (7)$$

At the high pressure, the rates of the energization and de-energization are relatively fast, which thus can be treated as fast pre-equilibrium steps. The rate determination step is the transformation of A^* into products.

Except for high vacuum systems, where isolated reactions may occur, the internal energy is always not fixed. A transition from microscopic to macroscopic description must be taken into consideration. If the rate of the reaction (3) is small as compared with the rates of the activation (1) and the deactivation (2), from Eq. (4) we have $dk_1(E)[A][M] = k_{-1}[A^*(E)][M]$. If we use $P(E)$ to denote the energy distribution function, then the $P(E)dE$ is the probability of finding an A molecule in the range of energy $[E, E + dE]$, i.e., $P(E)dE = [A(E)]/[A]$. Because A^* is A at the high energy, when E is large we have $P(E)dE = [A^*(E)]/[A]$ and [2] we get

$$\frac{dk_1(E)}{k_{-1}} = P(E)dE. \quad (8)$$

The rate coefficient counting all the energy (the so-called the thermal rate coefficient), k_{uni}^∞ , is the integration of Eq. (7) over the energy,

$$k_{\text{uni}}^\infty = \int_{E_0}^{\infty} k(E) P(E) dE, \quad (9)$$

where E_0 is the threshold energy, and $P(E)$ is BG distribution $P(E) = Q^{-1}N(E) \exp(-E/k_B T)$ with the density of states $N(E)$ and the partition function Q .

In the low pressure limit, the rate is given by a second order expression in $[A]$ and $[M]$, and thus from Eq. (6) we have the unimolecular reaction rate coefficient at the energy E [3],

$$k_{\text{uni}}^0(E) = \lim_{[M] \rightarrow 0} \frac{\nu}{[A][M]} = dk_1(E), \quad (10)$$

and the thermal rate coefficient is $k_{\text{uni}}^0 = k_1$. If the statistical property of the system is assumed to follow Boltzmann–Gibbs (BG) distribution [3], it is

$$k_{\text{uni}}^0 = k_1 = \frac{Z_{AM}}{Q} \int_{E_0}^{\infty} N(E) \exp\left(-\frac{E_0}{k_B T}\right) dE, \quad (11)$$

where Z_{AM} is the collision number between A and M per unit volume per unit time, Q is the partition function, $N(E)$ is the density of states of the reactant, k_B is the Boltzmann constant, and T is temperature.

There are many reaction rate theories that have been studied to obtain possible unimolecular reaction rate coefficients in the cases of both high pressure limit and low pressure limit. In all the traditional theories, just as that in Eq. (11), the energy distribution function $P(E)$ in Eq. (9) has always been assumed to be a BG distribution. These are only a good approximation in the situations when the statistical property of the system can be described by BG statistical mechanics. However, chemical

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