MICROCANONICAL ENERGY DISTRIBUTION IN COMPLEXES OF CLASSICAL OSCILLATORS

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Received April 21st, 1970

In the classical theory of unimolecular reactions based on the Kassel model[1,2], a significant role is played by the microcanonical distribution of energy in a complex of loosely coupled harmonic oscillators. This model involves the assumption that the energy of the complex can be expressed as the sum of energies of individual oscillators and that the energy of each oscillator may be expressed as the sum of two quadratic terms corresponding to the kinetic and potential energy. Further, it is assumed that the weak interaction of the oscillators representing a molecule results in a rapid mutual exchange of energy so that the equilibrium energy distribution is not disturbed by the reaction.

The probability $\varrho_0(\varepsilon_1, .. \varepsilon_s)\, \mathrm{d}\varepsilon_1 \ldots \mathrm{d}\varepsilon_s$ that in a microcanonical ensemble of complexes of s harmonic oscillators with a total vibrational energy ε to $\varepsilon + \mathrm{d}\varepsilon$ the energy of the first oscillator in an arbitrarily chosen complex is ε_1 to $\varepsilon_1 + \mathrm{d}\varepsilon_1$, that of the second oscillator ε_2 to $\varepsilon_2 + \mathrm{d}\varepsilon_2$ and so on ($\varepsilon \leqq \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_s \leqq \varepsilon + \mathrm{d}\varepsilon$) is given as

$$\varrho_0(\varepsilon_1, .. \varepsilon_s)\, \mathrm{d}\varepsilon_1 \ldots \mathrm{d}\varepsilon_s = \iint\limits_{p_1^2+q_1^2=\varepsilon_1}^{\varepsilon_1+\mathrm{d}\varepsilon_1} \mathrm{d}q_1\, \mathrm{d}p_1 \ldots \iint\limits_{p_s^2+q_s^2=\varepsilon_s}^{\varepsilon_s+\mathrm{d}\varepsilon_s} \mathrm{d}q_s\, \mathrm{d}p_s\, .$$

$$\cdot \left(\int \overset{s}{\underset{\mathrm{I}}{\cdots}} \int \iint\limits_{p_1^2+q_1^2=\varepsilon_1}^{\varepsilon_1+\mathrm{d}\varepsilon_1} \mathrm{d}q_1\, \mathrm{d}p_1 \ldots \iint\limits_{p_s^2+q_s^2=\varepsilon_s}^{\varepsilon_s+\mathrm{d}\varepsilon_s} \mathrm{d}q_s\, \mathrm{d}p_s \right)^{-1} = \Gamma(s)\, \mathrm{d}\varepsilon_1 \ldots \mathrm{d}\varepsilon_s / \varepsilon^{s-1}\, \mathrm{d}\varepsilon\, , \qquad (1)$$

where q_i and p_i are conjugated coordinates and momenta of the i-th oscillator, $\int \overset{s}{\underset{\mathrm{I}}{\cdots}} \int$ denotes the integration with respect to $\varepsilon_1, .. \varepsilon_s$ over the region of nonnegative values of ε_i restricted by the condition $\varepsilon < \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_s \leqq \varepsilon + \mathrm{d}\varepsilon$, and $\Gamma(s)$ denotes the gamma function (coefficients before q_i and p_i in Eq. (*1*) and others can be set equal to one without loss of generality[1]). A central role in the Kassel theory is played by the probability $p_0(\varepsilon)$ that in a microcanonical ensemble of s oscillators with the total vibrational energy ε to $\varepsilon + \mathrm{d}\varepsilon$ the energy of a certain, *e.g.* first oscillator in an arbitrarily chosen complex is larger than ε_0 while the energy distribution in the remaining oscillators is arbitrary:

$$p_0(\varepsilon) = \int_{\varepsilon_1=\varepsilon_0}^{\varepsilon} \int \overset{s-1}{\underset{\mathrm{II}}{\cdots}} \int \varrho_0(\varepsilon_1, .. \varepsilon_s)\, \mathrm{d}\varepsilon_1 \ldots \mathrm{d}\varepsilon_s = [(\varepsilon - \varepsilon_0)/\varepsilon]^{s-1}\, \eta(\varepsilon - \varepsilon_0)\, . \qquad (2)$$

Here $\int \overset{s-1}{\underset{\mathrm{II}}{\cdots}} \int$ denotes integration with respect to $\varepsilon_2, .. \varepsilon_s$ over the region of nonnegative values of

ε_i restricted by the condition $\varepsilon - \varepsilon_1 < \varepsilon_2 + \varepsilon_3 + \ldots + \varepsilon_s \leqq \varepsilon - \varepsilon_1 + \mathrm{d}\varepsilon$, and $\eta(\varepsilon - \varepsilon_0)$ denotes the step Heaviside function.

In Kassel's model the rate constant of dissociation of the complex with the energy ε is proportional to $p_0(\varepsilon)$, and ε_0 means the dissociation energy of the first oscillator. A molecule can therefore be represented by a system of s oscillators of which the first one is a so-called truncated[3] harmonic oscillator (Fig. 1) and the others are harmonic. It is natural to attribute to the undissociated molecule only that part of the phase space for which the coordinate q_1 is smaller than a certain critical extension q_0 $(= \varepsilon_0^{1/2})$. For the complex thus modified, the probabilities ϱ and p will be given by equations different from *(1)* and *(2)*.

The probability $\varrho(\varepsilon_1, \ldots \varepsilon_s)\, \mathrm{d}\varepsilon_1 \ldots \mathrm{d}\varepsilon_s$ can be calculated from an equation analogous to *(1)*; the difference is that the integration with respect to p_1 and q_1 is restricted by the conditions $\varepsilon_1 < p_1^2 + q_1^2 \leqq \varepsilon_1 + \mathrm{d}\varepsilon_1$, $q_1 < q_0$. The integral can be depicted geometrically as that part of the annular space (of radius $\varepsilon_1^{1/2}$ and width $\mathrm{d}\varepsilon_1/2\varepsilon_1^{1/2}$) where $q_1 < q_0$ $(= \varepsilon_0^{1/2})$ (Fig. 2):

$$\iint\limits_{\substack{p_1^2 + q_1^2 = \varepsilon_1 \\ q_1 < q_0 (= \varepsilon_0^{1/2})}}^{\varepsilon_1 + \mathrm{d}\varepsilon_1} \mathrm{d}q_1\, \mathrm{d}p_1 = \pi[1 - \arccos\,[(\varepsilon_0/\varepsilon_1)^{1/2}]\, \eta(\varepsilon_1 - \varepsilon_0)/\pi]\, \mathrm{d}\varepsilon_1\,, \tag{3}$$

where $\eta(\varepsilon_1 - \varepsilon_0)$ is the step function which is equal to one for $\varepsilon_1 > \varepsilon_0$ and equal to zero for $\varepsilon_1 < \varepsilon_0$. Thus we obtain

$$\varrho(\varepsilon_1, \ldots \varepsilon_s)\, \mathrm{d}\varepsilon_1 \ldots \mathrm{d}\varepsilon_s = [1 - \arccos\,[(\varepsilon_0/\varepsilon_1)^{1/2}]\, \eta(\varepsilon_1 - \varepsilon_0)/\pi]\, \mathrm{d}\varepsilon_1 \ldots \mathrm{d}\varepsilon_s\,.$$
$$.\left\{\int \overset{s}{\underset{\mathrm{I}}{\cdots}} \int [1 - \arccos\,[(\varepsilon_0/\varepsilon_1)^{1/2}]\, \eta(\varepsilon_1 - \varepsilon_0)/\pi]\, \mathrm{d}\varepsilon_1 \ldots \mathrm{d}\varepsilon_s\right\}^{-1}\,. \tag{4}$$

The s-fold integral in this equation can be reduced to a single one with the aid of the Laplace transformation:

$$\int \overset{s}{\underset{\mathrm{I}}{\cdots}} \int [1 - \arccos\,[(\varepsilon_0/\varepsilon_1)^{1/2}]\, \eta(\varepsilon_1 - \varepsilon_0)/\pi]\, \mathrm{d}\varepsilon_1 \ldots \mathrm{d}\varepsilon_s =$$
$$= \{\varepsilon^{s-1}/\Gamma(s) - (\varepsilon - \varepsilon_0)^{s-1}\, [\varepsilon_0/(\varepsilon - \varepsilon_0)]^{1/2}\, F[\varepsilon_0/(\varepsilon - \varepsilon_0)]\, \eta(\varepsilon - \varepsilon_0)/\pi\Gamma(s)\}\, \mathrm{d}\varepsilon\,, \tag{5}$$

where

$$F[\varepsilon_0/(\varepsilon - \varepsilon_0)] = \int_0^1 (1 - y^2)^{s-1}\, [y^2 + \varepsilon_0/(\varepsilon - \varepsilon_0)]^{-1}\, \mathrm{d}y\,. \tag{6}$$

For $(\varepsilon - \varepsilon_0)/\varepsilon \ll 1$ the following approximate expression holds:

$$\varrho(\varepsilon_1, \ldots \varepsilon_s) = \beta(\varepsilon)\, \varrho_0(\varepsilon_1, \ldots \varepsilon_s)\,, \tag{7}$$

where $\beta(\varepsilon)$ (this parameter can be considered as a correction factor) is

$$\beta(\varepsilon) \approx \{1 - [(\varepsilon_1 - \varepsilon_0)/\varepsilon_1]^{1/2}\, \eta(\varepsilon_1 - \varepsilon_0)/\pi\}/\{1 - [(\varepsilon - \varepsilon_0)/\varepsilon]^{s-1}\,.$$
$$.\, [(\varepsilon - \varepsilon_0)/\varepsilon_0]^{1/2}\, \Gamma(\tfrac{1}{2})\, \Gamma(s)\, \eta(\varepsilon - \varepsilon_0)/2\pi\Gamma(s + \tfrac{1}{2})\}\,. \tag{8}$$

TABLE I

Values of the Correction Factor $\gamma(\varepsilon)$ Calculated from Equation (*11*)

	$(\varepsilon - \varepsilon_0)/\varepsilon_0$	0·05	0·10	0·15	0·20
$\gamma(\varepsilon)$	$s = 5$	0·971	0·959	0·950	0·942
	$s = 10$	0·980	0·971	0·965	0·960

The probability $p(\varepsilon)$ can be expressed by an equation analogous to (*2*):

$$p(\varepsilon) = \int_{\varepsilon_0}^{\varepsilon} \mathrm{d}\varepsilon_1 \int^{s-1}_{\mathrm{II}} \cdots \int \varrho(\varepsilon_1, \ldots \varepsilon_s) \, \mathrm{d}\varepsilon_2 \ldots \mathrm{d}\varepsilon_s \, . \tag{9}$$

This s-fold integral can be reduced to

$$p(\varepsilon) = \gamma(\varepsilon) \, p_0(\varepsilon) \, , \tag{10}$$

where

$$\gamma(\varepsilon) = [1 - \varkappa(\varepsilon)]/[1 - \varkappa(\varepsilon) \, p_0(\varepsilon)] \, , \tag{11}$$

$$\varkappa(\varepsilon) = F[\varepsilon_0/(\varepsilon - \varepsilon_0)] \, [\varepsilon_0/(\varepsilon - \varepsilon_0)]^{1/2} \, \eta(\varepsilon - \varepsilon_0)/\pi \, . \tag{12}$$

Since $p_0(\varepsilon) < 1$, also $\gamma(\varepsilon) < 1$. For $(\varepsilon - \varepsilon_0)/\varepsilon \ll 1$ the following approximate expression holds

$$\varkappa(\varepsilon) \approx [(\varepsilon - \varepsilon_0)/\varepsilon_0]^{1/2} \, \Gamma(\tfrac{1}{2}) \, \Gamma(s) \, \eta(\varepsilon - \varepsilon_0)/2\pi \Gamma(s + \tfrac{1}{2}) \, . \tag{13}$$

Numerical calculation shows that the $\gamma(\varepsilon)$ values for energies not too larger than ε_0 are only little different from unity, hence also the $p(\varepsilon)$ values differ only little from $p_0(\varepsilon)$ (Table I). In thermal

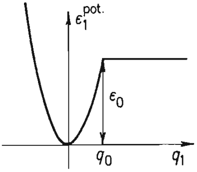

FIG. 1

Potential Energy Diagram of Truncated Harmonic Oscillator

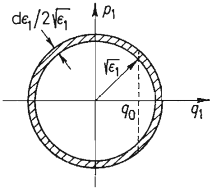

FIG. 2

Region of Integration

dissociations, an important role is played only by molecules with energy values close to $\varepsilon = \varepsilon_0 + (s - 1) kT$, for which the $(\varepsilon - \varepsilon_0)/\varepsilon_0$ value is close to $(s - 1) kT/\varepsilon_0$; the latter is in the case of dissociation of moderately large molecules usually much smaller than unity and the approximation (*13*) is adequate. The correction factor for the phase integral then is $1 - \exp(-\varepsilon_0/kT) : 2(\pi\varepsilon_0/kT)^{1/2}$ (*cf.*[4,5]) and for the canonical (high-pressure) rate constant k_∞ is $1 - [2(\pi\varepsilon_0 : kT)^{1/2}]^{-1}$. The value of the former is actually equal to one; the value of the latter is 0·96 (for the usual value of $\varepsilon_0/kT = 40$). In these cases the use of $p_0(\varepsilon)$ is justified since the correction is small. However, the correction is not negligible in the case of systems obtained in a way other than thermal activation, when the total energy ε can be much larger than the dissociation energy.

REFERENCES

1. Kassel L. S.: *Kinetics of Homogeneous Gas Reactions.* Chemical Catalog, New York 1932.
2. Nikitin E. E.: *Theory of Thermally Induced Gas Phase Reactions.* Indiana University Press, Bloomington 1966.
3. Kondraťev V. N.: *Chemical Kinetics of Gas Reactions,* p. 297. Pergamon Press, Oxford 1964.
4. Slater N. B.: Proc. Leeds Phil. Soc. (Sci.) *6*, 268 (1955).
5. Slater N. B.: *Theory of Unimolecular Reactions*, p. 120. Cornell University Press, Ithaca 1959.

Translated by K. Micka.