Chemical dynamics
CHEM674

Applications of Transition State Theory
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Outline

- Statistical approach to reaction dynamics transition state theory
  - Motion on the potential surface
  - Basic postulates and derivation of transition state theory
  - Dynamical derivation of transition state theory
  - Quantum mechanical effects in transition state theory
  - Thermodynamic formulation of transition state theory
- Application of transition state theory
  - Evaluating partition functions by statistical mechanics
  - Electronic partition function
  - Translational partition function
  - Vibrational partition function
  - Rotational partition function

Evaluating partition functions by statistical mechanics

Suppose the bimolecular reaction :

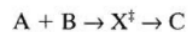$$A + B \rightarrow X^{\ddagger} \rightarrow C$$
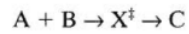
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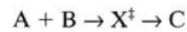$$A + B \rightarrow X^{\ddagger} \rightarrow C$$

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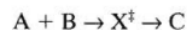
Calculating the rate constant for a reaction requires that we know how to evaluate the partition functions that arise in the transition state theory derivation.

Real molecules may have rotational, vibrational, electronic and translational energies. Therefore, the total partition function associated with the internal motion for each molecule is given by the product of partitions functions associated with each component :

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To calculate the individual partition functions, one needs to know :

-    Moments of inertia
-    Vibrational frequencies
-    Electronic states

Electronic partition function

The electronic partition function is given by

$$Q_{elec} = \sum_i g_i e^{-E_i/k_B T}$$

Where g_i is the degeneracy and E_i is the energy above the lowest state of the system. In most reactions, few electronic energy levels other than the ground state need to be considered.

Translational partition function

For the translational motion for a particle of mass m moving in a one-dimensional box of length l, the energy derived from the Schrödinger equation is

$$E_n = \frac{n^2 h^2}{8ml^2}$$

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When the energy levels are closely spaced, $E_{n+1} - E_n = (h^2/8ml^2)(2n + 1)$ is $\ll k_B T$

The sum can be replaced by an integral:

$$Q_{trans} = \int_0^{\infty} \exp\left(\frac{-n^2 h^2}{8ml^2 k_B T}\right) dn$$

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$$E_{trans} = E_{trans,x} + E_{trans,y} + E_{trans,z}$$

$$Q_{trans} = Q_{trans,x} Q_{trans,y} Q_{trans,z}$$

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A polyatomic molecule has s=$3N - 6$ vibrational modes if is nonlinear and $3N - 5$ modes if it is linear; therefore, the vibrational partition function for a polyatomic molecule is

$$Q_{vib} = \prod_{i=1}^{s} \frac{1}{1 - \exp(-hc\bar{\nu}_i/k_B T)}$$

Rotational partition function

For a linear rigid rotor, the energy levels are given by

$$E_J \approx \frac{J(J+1)\hbar^2}{2I}$$

Where $\hbar^2/2I$ is the rotational constant and $J=0,1,2,...$ is a rotational quantum number. The multiplicity of each level is 2J+1, so

$$Q_{rot} = \sum_0^\infty (2J+1)\exp[-J(J+1)\hbar^2/2Ik_BT]$$

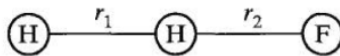If the level intervals are small compared to k_BT, the sum can be replaced by an integral:

$$Q_{rot} = \int_0^\infty (2J+1)\exp[-J(J+1)\hbar^2/2Ik_BT]dJ \quad \Longrightarrow \quad Q_{rot} = \frac{8\pi^2 I k_B T}{h^2}$$

The latter is also a reasonably good approximation for real nonrigid molecules. For a polyatomic molecules with moments of intertia I_a, I_b and I_c about is principal axes, the rotational partition function is

$$Q_{rot} = \pi^{1/2}\left(\frac{8\pi^2 I_a k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_b k_B T}{h^2}\right)^{1/2}\left(\frac{8\pi^2 I_c k_B T}{h^2}\right)^{1/2}$$

In class exercise: F + H$_2$ reaction

Consider a linear activated complex

Parameters	F$\cdots$H$_a$—H$_b$	F	H$_2$
r_2(F—H),Å	1.602		
r_1(H—H),Å	0.756		r(H—H) = 0.7417Å
$\bar{\nu}_1$, cm^{-1}	4007.6		4395.2
$\bar{\nu}_2$, cm^{-1}	397.9		
$\bar{\nu}_3$, cm^{-1}	397.9		
$\bar{\nu}_4$, cm^{-1}	310.8i		
E_a(kJ/mole)	6.57		
m(amu)	21.014	18.9984	2.016
I(amu Å^2)	7.433		0.277
g_{elec}	2	4	1

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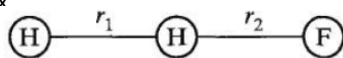$$Q_{rot} = \frac{8\pi^2 I k_B T}{h^2} \qquad Q_{vib} = \prod_{i=1}^s \frac{1}{1 - \exp(-hc\bar{\nu}_i/k_B T)} \qquad Q_{elec} = \sum_i g_i e^{-E_i/k_B T}$$

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