

Kinetics Theory

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1 Canonical TST

$$k(T) = \kappa(T) \frac{k_B T}{h} \frac{m}{m^\ddagger} \frac{Q^\ddagger}{Q_{\text{react}}} e^{-E/k_B T} \quad (1)$$

2 Microcanonical TST

$$k(E) = \frac{N^\ddagger(E)}{h\rho(E)} \quad (2)$$

3 Partition Functions

Generally use rigid-rotor, harmonic oscillator (RRHO) approximations to determine the partition functions

Generally use discrete partition function

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

It is assumed that all of the components of Q are separable

$$Q = q_{\text{vib}} q_{\text{rot}} q_{\text{trans}} q_{\text{elec}}$$

where q_{vib} , q_{rot} , q_{trans} , q_{elec} are the partition functions describing the vibrational, rotational, translation, and electronic energy levels, respectively.

3.1 Vibrational

The vibrational partition function is often assumed with a harmonic oscillator models, where each vibration is an uncoupled harmonic oscillator with energy levels:

$$E_{\text{vib}} = h\omega$$

where ω is the frequency of vibration. Therefore we can get the partition function for a *specific* vibration where each level is equally spaced (i.e., $E_{\text{vib},n} = nh\omega$ for the n -th vibrational state of

mode with frequency ω):

$$\begin{aligned} q_{vib} &= \sum_{n=1}^{\infty} e^{-E_{vib,n}/k_B T} \\ &= \sum_{n=1}^{\infty} e^{-nh\omega/k_B T} \\ &= \sum_{n=1}^{\infty} (e^{-h\omega/k_B T})^n \end{aligned}$$

This equation can be recast by recognizing that we have a convergent infinite series:

$$q_{vib} = \frac{1}{1 - e^{-h\omega/k_B T}}$$

To get the overall vibrational partition function, we note that the levels are uncoupled, and are thus separable. Hence, the total partition function is the product of the partition functions for each vibration:

$$\begin{aligned} Q_{vib_{total}} &= \prod_i^{N_{vib}} q_{vib,i} \\ &= \prod_i^{N_{vib}} \frac{1}{1 - e^{-h\nu_i/k_B T}} \end{aligned}$$

3.2 Rotational

$$E_{rot} = BJ(J+1)$$

3.3 Translational

3.4 Electronic

4 Projections

A projection operator is constructed

5 Instructions