STATISTICAL MOLECULAR THERMODYNAMICS

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Video 3.7

The Molecular Partition Function

RELATIONSHIP BETWEEN Q AND q

The probability that a *member of an ensemble* is in quantum state j is:

$$p_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}}$$

ensemble energy

molecular energy

Similarly the probability (π_j) that a *molecule* is in its jth molecular energy state is:

$$\pi_j = \frac{e^{-\beta \varepsilon_j}}{\sum_j e^{-\beta \varepsilon_j}}$$

By analogy, the probability that a molecule is in some *vibrational state* can be written as:

$$\pi_j^{vib} = \frac{e^{-\beta \varepsilon_j^{vib}}}{\sum_j e^{-\beta \varepsilon_j^{vib}}}$$

We can write the same types of expressions for *elec*, *trans*, and *rot* degrees of freedom

FURTHER ANALOGIES

$$\left\langle \varepsilon^{vib} \right\rangle = \sum_j \pi_j^{vib} \varepsilon_j^{vib} = \sum_j \varepsilon_j^{vib} \frac{e^{-\beta \varepsilon_j^{vib}}}{\sum_j e^{-\beta \varepsilon_j^{vib}}} = \sum_j \varepsilon_j^{vib} \frac{e^{-\beta \varepsilon_j^{vib}}}{q_{vib}}$$

$$= -\frac{\partial \ln q_{vib}}{\partial \beta} = k_B T^2 \frac{\partial \ln q_{vib}}{\partial T}$$

$$\left\langle \varepsilon^{elec} \right\rangle = k_B T^2 \frac{\partial \ln q_{elec}}{\partial T} \qquad \left\langle \varepsilon^{vib} \right\rangle = k_B T^2 \frac{\partial \ln q_{vib}}{\partial T}$$

$$\left\langle \varepsilon^{rot} \right\rangle = k_B T^2 \frac{\partial \ln q_{rot}}{\partial T} \qquad \left\langle \varepsilon^{trans} \right\rangle = k_B T^2 \frac{\partial \ln q_{trans}}{\partial T}$$

THE MOLECULAR PARTITION FUNCTION

The energy of a molecule is composed of translational, rotational, vibrational, and electronic components according to:

$$\varepsilon = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec}$$

Leading to a molecular partition function:

$$q(V,T) = \sum_j e^{-\beta\left(\varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec}\right)_j}$$

$$= \sum_i e^{-\beta\varepsilon_{trans,i}} \sum_j e^{-\beta\varepsilon_{rot,j}} \sum_k e^{-\beta\varepsilon_{vib,k}} \sum_l e^{-\beta\varepsilon_{elec,l}}$$

$$= q_{trans} q_{rot} q_{vib} q_{elec}$$

DEGENERACY

Partition functions can be written as summations over *states*. Each state is associated with a wave function having a corresonding *energy*. States that have the *same energy* are called *levels*. The number of different wave functions that have the *same energy for a given level* is called the *degeneracy g*.

$$q(V,T) = \sum_{j(states)} e^{-\beta \varepsilon_j}$$

terms representing a degenerate level are repeated g_j times

$$q(V,T) = \sum_{j(levels)} g_j e^{-\beta \varepsilon_j}$$

terms representing a degenerate level are written once and multiplied by g_j

This expression is more convenient to use in future manipulations.

E.g., Rotational Partition Function

For allowed rotational energies for a linear molecular we have:

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1) \quad J = 0,1,2,\ldots$$

$$g_J = 2J + 1$$

So,

$$q_{\text{rot}}(V,T) = \sum_{j(\text{states})} e^{-\beta \varepsilon_j} = e^{-\varepsilon_{J=0}/k_\text{B}T} + e^{-\varepsilon_{J=1}/k_\text{B}T} + e^{-\varepsilon_{J=1}/k_\text{B}T} + e^{-\varepsilon_{J=1}/k_\text{B}T} + \ldots$$

$$q_{\text{rot}}(V,T) = \sum_{j(\text{levels})} g_j e^{-\beta \varepsilon_j} = 1e^{-\varepsilon_{J=0}/k_\text{B}T} + 3e^{-\varepsilon_{J=1}/k_\text{B}T} + \ldots$$

more convenient to denote explicitly the degeneracy