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5.62 Physical Chemistry II
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5.62 Lecture #7: Translational Part of Boltzmann Partition Function

CANONICAL PARTITION FUNCTION FOR INDEPENDENT, INDISTINGUISHABLE MOLECULES

$$Q(N, V, T) = q^N / N!$$

approximation valid for $q \gg N$, not assured to be always valid
“corrected Boltzmann statistics”

where $q = \sum_i e^{-\epsilon_i / kT}$ molecular partition function
sum over states of *one* of the molecules

GOAL: to determine for what systems $q \gg N$ is valid.

PROCEDURE: 1) develop a (simplified) physical picture for q
2) calculate a value for q

1) PROPERTIES OF q

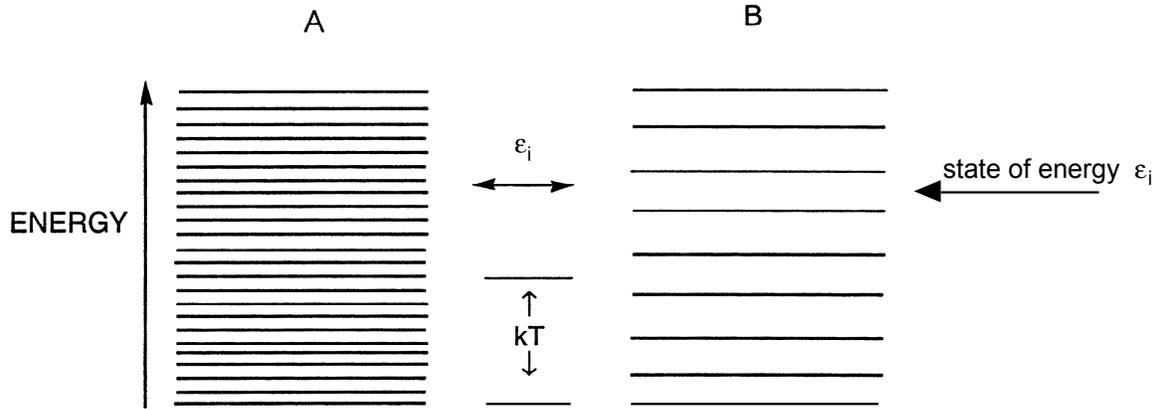
q is a measure of the total number of molecular states available to one molecule at some temperature.

$e^{-\epsilon_i / kT}$ proportional to population in state i at T

$q \approx$ total # of states accessible at T

population in single-particle state i in N atom system: $N(e^{-\epsilon_i / kT} / q)$

where the term in parentheses is the probability of finding any single particle in state i .
Consider molecules A and B with energy levels sketched below.



1. Molecule A has more states because they are more closely spaced in energy.
2. The total number of thermally accessible states in molecule A is larger because there are more states with ϵ_i less than or comparable to kT . Contribution of each state to the sum in the definition of q depends on its energy relative to kT .

$$(kT \text{ is an energy}) \quad (k = 1.38 \times 10^{-23} \text{ J/K})$$

Therefore

$$q_A > q_B$$

So, q plays an essential role in determining the probability that a molecule is in state i .

$$\text{Since } \bar{n}_i = \frac{N e^{-\epsilon_i/kT}}{q}$$

$$\frac{\bar{n}_i}{N} = P_i = \frac{e^{-\epsilon_i/kT}}{q} = \frac{e^{-\epsilon_i/kT}}{\sum_m e^{-\epsilon_m/kT}}$$

↑
probability of finding molecule in state i

P_i depends not only on the energy of the i -th state, ϵ_i , relative to kT , but on q , the total number of states accessible.

$$P_i = \frac{e^{-\epsilon_i/kT}}{q} = \frac{e^{-\epsilon_i/kT}}{\sum_m e^{-\epsilon_m/kT}}$$

BOLTZMANN DISTRIBUTION FUNCTION

Consider molecules A and B again. Both A and B have a state i at energy ϵ_i . Therefore

Probability of molecule A in state i Probability of molecule B in state i

$$P_i^A = \left(\frac{\bar{n}_i}{N} \right)_A = \frac{e^{-\varepsilon_i/kT}}{q_A} \quad P_i^B = \left(\frac{\bar{n}_i}{N} \right)_B = \frac{e^{-\varepsilon_i/kT}}{q_B}$$

It follows that

$$\frac{P_i^A}{P_i^B} = \frac{q_B}{q_A} < 1$$

Probability of molecule A being in state i with energy ε_i is less than probability of molecule B being in state i with energy ε_i because there are more states in molecule A.

Consider the same molecule A. The ratio of the probabilities of finding A in two states j and k or the ratio of populations in the two states j and k are

$$\frac{P_j^A}{P_k^A} = \frac{\bar{n}_j^A}{\bar{n}_k^A} = \frac{e^{-\varepsilon_j/kT} / q_A}{e^{-\varepsilon_k/kT} / q_A} = e^{-(\varepsilon_j - \varepsilon_k)/kT}$$

What happens to q as $T \rightarrow 0$? What happens to all P_j ?

2. CALCULATION OF q

NEED: ε_i , the energies of the states of a molecule: translation, rotation, vibration, electronic.

START: with the energies of the translational states to calculate q_{trans}

$$q_{\text{trans}}$$

TRANSLATIONAL MOLECULAR PARTITION FUNCTION

The ε_i for translational states are solutions to the Schrödinger equation for a particle in a box.

The translational energy of a particle of mass m contained in a box of dimensions a, b, c with quantum numbers L, M, N is

$$\varepsilon(L,M,N) = \frac{h^2}{8m} \left[\frac{L^2}{a^2} + \frac{M^2}{b^2} + \frac{N^2}{c^2} \right]$$

$$q_{\text{trans}} = \sum e^{-\epsilon(L,M,N)/kT}$$

$$q_{\text{trans}} = \sum_{L=1}^{\infty} \sum_{M=1}^{\infty} \sum_{N=1}^{\infty} \exp\left[\frac{-h^2}{8mkT}\left(\frac{L^2}{a^2} + \frac{M^2}{b^2} + \frac{N^2}{c^2}\right)\right]$$

$$= \left[\sum_{L=1}^{\infty} \exp\left(\frac{-h^2 L^2}{8mkT a^2}\right)\right] \left[\sum_{M=1}^{\infty} \exp\left(\frac{-h^2 M^2}{8mkT b^2}\right)\right] \left[\sum_{N=1}^{\infty} \exp\left(\frac{-h^2 N^2}{8mkT c^2}\right)\right]$$

Need to evaluate sums

$$\sum_{L=1}^{\infty} \exp\left(\frac{-h^2 L^2}{8mkT a^2}\right) = \sum_{L=0}^{\infty} \exp\left(\frac{-h^2 L^2}{8mkT a^2}\right) - 1 \approx \sum_{L=0}^{\infty} \exp\left(\frac{-h^2 L^2}{8mkT a^2}\right)$$

Now $\frac{h^2}{8mkT a^2} \ll 1$ States are closely spaced in energy.
Approximate sum by an integral.

$$\sum_{L=0}^{\infty} \exp\left(\frac{-h^2 L^2}{8mkT a^2}\right) \approx \int_0^{\infty} dL \exp\left(\frac{-h^2 L^2}{8mkT a^2}\right) = \int_0^{\infty} dL \exp(-g^2 L^2) = \frac{\pi^{1/2}}{2g}$$

$$\int_0^{\infty} e^{-g^2 x^2} dx = \frac{\pi^{1/2}}{2g} \quad \text{with} \quad g = \left(\frac{h^2}{8mkT a^2}\right)^{1/2}$$

Therefore $\int_0^{\infty} dL \exp\left(\frac{-h^2 L^2}{8mkT a^2}\right) = \left(\frac{8\pi a^2 mkT}{4h^2}\right)^{1/2}$

so

$$q_{\text{trans}} = \left(\frac{2\pi a^2 mkT}{h^2}\right)^{1/2} \left(\frac{2\pi b^2 mkT}{h^2}\right)^{1/2} \left(\frac{2\pi c^2 mkT}{h^2}\right)^{1/2}$$

$$q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} abc = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

We have evaluated q_{trans} in terms of quantities we can know!!

What idealizations, if any, have we made?

CHECK VALIDITY CONDITION FOR BOLTZMANN STATISTICS, $q_{\text{trans}} \gg N$.

Calculate q_{trans} for N_2 , 1 atm pressure, 1 mole, 273K

$$m = \frac{28 \text{ g/mol} \times 10^{-3} \text{ kg/g}}{6.0 \times 10^{23} \text{ mol}^{-1}} = 4.67 \times 10^{-26} \text{ kg}$$

$$h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s} \quad k = 1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$$

$$T = 273 \text{ K} \quad V = 22.4 \text{ liters} = 22.4 \times 10^{-3} \text{ m}^3$$

Unit check:

$$\left(\frac{2\pi mkT}{h^2} \right)^{3/2} V = \left(\frac{\text{kgJK}^{-1}\text{K}}{\text{J}^2\text{s}^2} \right)^{3/2} \text{m}^3 = \left(\frac{\text{kg} \cdot \text{K}^{-1} \cdot \text{K}}{\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2} \cdot \text{s}^2} \right)^{3/2} \text{m}^3$$

$$\left(\frac{1}{\text{m}^2} \right)^{3/2} \text{m}^3 \quad \text{UNITLESS}$$

Plugging numbers for N_2 @ 273K, 1 atm, 1 mole into q_{trans} yields:

$$q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V = 2.8 \times 10^{30}$$

Check condition for Boltzmann statistics, $q \gg N$

For 1 mole of N_2 (in our volume of 22.4 liters), $N = 6 \times 10^{23}$

$$\frac{N}{q} = \frac{6 \times 10^{23}}{2.8 \times 10^{30}} = 2.1 \times 10^{-7} \ll 1 \text{ as required}$$

So $\bar{n}_i = \frac{N}{q} e^{-\epsilon_i/kT} < 10^{-7}$ because $e^{-\epsilon_i/kT} < 1$ always

- on average, less than 10^{-7} molecules per state
- probability of more than 1 molecule in any state is very small (what is the probability of finding 2 or more molecules in the ϵ_i level?)
- corrected Boltzmann statistics OK for molecules at $T > 300\text{K}$

Always use simple short cuts to avoid repetitive calculations.

E.g. decrease T from 273K to 1 K

$$q(1\text{K}) = q(273\text{K}) \left[\frac{1}{273} \right]^{3/2}$$

decrease V from 22.4L = $2.24 \times 10^4 \text{ cm}^3$ to 1 cm^3

$$q(1 \text{ cm}^3) = q(22.4\text{L}) \left[\frac{1}{2.24 \times 10^4} \right]$$

Check condition for corrected Boltzmann statistics, $q > N$, for 1 mole of *electrons* in $V = 22.4$ liters at $T = 273\text{K}$.

All parameters are the same as in N_2 calculation *except for mass*

$$m_e = 0.0005 \text{ g} \cdot \text{mol}^{-1}$$

$$\text{Since } q \propto m^{3/2} \quad : \quad \frac{q_{\text{trans}}^{e^-}}{q_{\text{trans}}^{\text{N}_2}} = \left(\frac{m_e}{m_{\text{N}_2}} \right)^{3/2}$$

$$q_{\text{trans}}^{e^-} = \left(\frac{0.0005}{28} \right)^{3/2} \frac{2.81 \times 10^{30}}{q_{\text{trans}}^{\text{N}_2}} = 2.4 \times 10^{23}$$

$$\text{So } \frac{N}{q} = \frac{6 \times 10^{23}}{2.4 \times 10^{23}} \text{ not } \ll 1 \quad !$$

Can't use corrected Boltzmann statistics for electrons at $T = 273\text{K}$.

Must use "Fermi-Dirac" statistics! At what T is Boltzmann statistics OK for an electron?

Since corrected Boltzmann statistics are valid for atoms and molecules under the vast majority of conditions, we can now calculate Q, the canonical partition function for indistinguishable molecules.

Fermi-Dirac (fermions) and Bose-Einstein (bosons) statistics next lecture.