Statistical Molecular Thermodynamics

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Video 4.2

Ideal Monatomic Gas: Q

Monatomic Ideal Gas Partition Function

We consider each *degree of freedom* separately:

For an ideal *monatomic* gas the *only* degrees of freedom are translational and electronic (a significant simplification):

The Energy: $$\varepsilon_{\text{atomic}} = \varepsilon_{\text{trans}} + \varepsilon_{\text{elec}} \quad \text{(sum)}$$

total energy

translational energy (*already done*)

electronic energy

Monatomic Ideal Gas: q_{elec}

We start from the usual expression for q, but summed over levels instead of states:

$$q_{\text{elec}} = \sum_{i}^{\text{levels}} g_i e^{-\beta\varepsilon_i}$$

energy of level i

degeneracy of level i

We can choose to set the lowest (ground) electronic energy state at zero, $\varepsilon_1 = 0$ (because in thermodynamics, zero is nearly always arbitrary), in which case:

$$q_{\text{elec}}(T) = g_1 + g_2 e^{-\beta\varepsilon_2} + g_3 e^{-\beta\varepsilon_3} + \cdots$$

Note: a function of T only

energy of level 2 *relative to the ground state energy*, $(\varepsilon_1 = 0)$

q_{elec} Is a Rapidly Convergent Sum

The electronic energy levels are spaced far apart, and therefore *we only need to consider the first one or two terms in the series*,

$$q_{\text{elec}}(T) = g_1 + g_2 e^{-\beta\varepsilon_2} + g_3 e^{-\beta\varepsilon_3} + \cdots$$

terms are getting small rapidly ⟶

General rule to remember:

At 300 K, you only need to keep terms where $\varepsilon_j < 10^3\ \text{cm}^{-1}$ $\longrightarrow$ $\left(e^{-\beta\varepsilon_j} > 0.008\right)$

Electronic Energy Levels

$$q_{\text{elec}}(T) = g_1 + g_2 e^{-\beta\varepsilon_2} + g_3 e^{-\beta\varepsilon_3} + \cdots$$

Note general trends,

- Noble gas atoms:
  $\varepsilon_2 \approx 10^5\ \text{cm}^{-1}$ (at 300 K, only 1st term)

- Alkali metal atoms:
  $\varepsilon_2 \approx 10^4\ \text{cm}^{-1}$ (at 300 K, only 1st term)

- Halogen atoms:
  $\varepsilon_2 \approx 10^2\ \text{cm}^{-1}$ (at 300 K, 1st *and* 2nd terms)

TABLE 4.1
Some atomic energy levels.[a]

Atom	Electron configuration	Degeneracy $g_e = 2J+1$	Energy/cm^{-1}
H	$1s$	2	0.
	$2p$	2	82 258.907
	$2s$	2	82 258.942
	$2p$	4	82 259.272
He	$1s^2$	1	0.
	$1s2p$	3	159 850.318
		1	166 271.70
Li	$1s^2 2s$	2	0.
	$1s^2 2p$	2	14 903.66
		4	14 904.00
	$1s^2 3s$	2	27 206.12
F	$1s^2 2s^2 2p^5$	4	0.
		2	404.0
	$1s^2 2s^2 2p^4 3s$	6	102 406.50
		4	102 681.24
		2	102 841.20
		4	104 731.86
		2	105 057.10

[a] From C.E. Moore, "Atomic Energy Levels" *Natl. Bur. Std, Circ.* 1 467, U.S. Government Printing Office, Washington D.C., 1949

The Simplest Partition Function

In general, for non-metals, it is sufficient to keep only the first two terms for $q_{\text{elec}}(T)$,

$$q_{\text{elec}}(T) \approx g_1 + g_2 e^{-\beta\varepsilon_2}$$

However, one should always keep in mind that for very high temperatures (like on the sun), or smaller values of ε_j (like in metals), additional terms may contribute. If one finds that the second term is of reasonable magnitude (>1% of the first term), then one should check to see that the third term can indeed be neglected. Atomic energy levels are known from experiment or available from quantum chemical computation.

Monatomic Ideal Gas Q

Thus, with both component partition functions in hand, we have for a *monatomic ideal gas*:

$$Q(N,V,T) = \frac{\left[q_{\text{trans}}(V,T)\,q_{\text{elec}}(T)\right]^N}{N!}$$

where $$q_{\text{trans}}(V,T) = \left(\frac{2\pi m k_{\text{B}} T}{h^2}\right)^{3/2} V$$

$$q_{\text{elec}}(T) \approx g_1 + g_2 e^{-\beta\varepsilon_2}$$