

The probability that the translational orbital n is occupied, irrespective of the state of internal motion of the molecule, is given by the ratio of the term in λ to the Gibbs sum \mathcal{Z} :

$$f(\epsilon_n) = \frac{\lambda Z_{\text{int}} \exp(-\epsilon_n/\tau)}{1 + \lambda Z_{\text{int}} \exp(-\epsilon_n/\tau)} \simeq \lambda Z_{\text{int}} \exp(-\epsilon_n/\tau). \quad (46)$$

The classical regime was defined earlier as $f(\epsilon_n) \ll 1$. The result (46) is entirely analogous to (13) for the monatomic case, but λZ_{int} now plays the role of λ .

Several of the results derived for the monatomic ideal gas are different for the polyatomic ideal gas:

(a) Equation (17) for λ is replaced by

$$\lambda = n/(n_Q Z_{\text{int}}), \quad (47)$$

with n_Q defined exactly as before. (We shall always use n_Q as defined for the monatomic ideal gas of atoms with zero spin.) Because $\lambda \equiv \exp(\mu/\tau)$ we have

$$\mu = \tau [\log(n/n_Q) - \log Z_{\text{int}}]. \quad (48)$$

(b) The free energy is increased by, for N molecules,

$$F_{\text{int}} = -N\tau \log Z_{\text{int}}. \quad (49)$$

(c) The entropy is increased by

$$\sigma_{\text{int}} = -(\partial F_{\text{int}}/\partial \tau)_V. \quad (50)$$

The former result $U = \frac{3}{2}N\tau$ applies to the translational energy alone.

Example: Spin entropy in zero magnetic field. Consider an atom of spin I , where I may represent both electronic and nuclear spins. The internal partition function associated