

Chemical Potential of Ideal Gas with Internal Degrees of Freedom

We consider now an ideal gas of identical polyatomic molecules. Each molecule has rotational and vibrational degrees of freedom in addition to the translational degrees of freedom. The total energy ε of the molecule is the sum of two independent parts,

$$\varepsilon = \varepsilon_n + \varepsilon_{\text{int}}, \quad (40)$$

where ε_{int} refers to the rotational and vibrational degrees of freedom and ε_n to the translational motion of the center of mass of the molecule. The vibrational energy problem is the harmonic oscillator problem treated earlier. The rotational energy was the subject of Problem 3.6.

In the classical regime the Gibbs sum for the orbital n is

$$\mathcal{Z} = 1 + \lambda \exp(-\varepsilon_n/\tau), \quad (41)$$

where terms in higher powers of λ are omitted because the average occupancy of the orbital n is assumed to be $\ll 1$. That is, we neglect the terms in \mathcal{Z} which correspond to occupancies greater than unity. In the presence of internal energy states the Gibbs sum associated with the orbital n becomes

$$\mathcal{Z} = 1 + \lambda \sum_{\text{int}} \exp[-(\varepsilon_n + \varepsilon_{\text{int}})/\tau], \quad (42)$$

or

$$\mathcal{Z} = 1 + \lambda \exp(-\varepsilon_n/\tau) \sum_{\text{int}} \exp(-\varepsilon_{\text{int}}/\tau). \quad (43)$$

The summation is just the partition function of the internal states:

$$Z_{\text{int}} = \sum_{\text{int}} \exp(-\varepsilon_{\text{int}}/\tau), \quad (44)$$

which is related to the internal free energy of the one molecule by $F_{\text{int}} = -\tau \log Z_{\text{int}}$. From (43) the Gibbs sum is

$$\mathcal{Z} = 1 + \lambda Z_{\text{int}} \exp(-\varepsilon_n/\tau). \quad (45)$$