24.5: The Partition Function for A Gas of Indistinguishable, Non-interacting, Separable-modes Molecules

We represent the successive molecular energy levels as ϵ_i and the successive translational, rotational, vibrational, and electronic energy levels as $\epsilon_{t,a}$, $\epsilon_{r,b}$, $\epsilon_{v,c}$, and $\epsilon_{e,d}$. Now the first subscript specifies the energy mode; the second specifies the energy level. We approximate the successive energy levels of a diatomic molecule as

$$\epsilon_1 = \epsilon_{t,1} + \epsilon_{r,1} + \epsilon_{v,1} + \epsilon_{e,1}$$

$$\epsilon_2 = \epsilon_{t,2} + \epsilon_{r,1} + \epsilon_{v,1} + \epsilon_{e,1}$$

$$\ldots$$

$$\epsilon_i = \epsilon_{t,a} + \epsilon_{r,b} + \epsilon_{v,c} + \epsilon_{e,d}$$

$$\ldots$$

In Section 22.1, we find that the partition function for the molecule becomes

$$z = \sum_{a=1}^{\infty}\sum_{b=1}^{\infty}\sum_{c=1}^{\infty}\sum_{d=1}^{\infty} g_{t,a}g_{r,b}g_{v,c}g_{e,d} \times \exp\left[\frac{-\left(\epsilon_{t,a}+\epsilon_{r,b}+\epsilon_{v,c}+\epsilon_{e,d}\right)}{kT}\right]$$

$$= z_t z_r z_v z_e$$

where z_t, z_r, z_v, and z_e are the partition functions for the individual kinds of motion that the molecule undergoes; they are sums over the corresponding energy levels for the molecule. This is essentially the same argument that we use in Section 22.1 to show that the partition function for an N-molecule system is a product of N molecular partition functions:

$$Z = z^N.$$

We are now able to write the partition function for a gas containing N molecules of the same substance. Since the molecules of a gas are indistinguishable, we use the relationship

$$Z_{\text{indistinguishable}} = \frac{1}{N!}z^N = \frac{1}{N!}\left(z_t z_r z_v z_e\right)^N$$

To make the notation more compact and to emphasize that we have specialized the discussion to the case of an ideal gas, let us replace "$Z_{\text{indistinguishable}}$" with "$Z_{\text{IG}}$". Also, recognizing that $N!$ enters the relationship because of molecular indistinguishability, and molecular indistinguishability arises because of translational motion, we regroup the terms, writing

$$Z_{\text{IG}} = \left[\frac{\left(z_t\right)^N}{N!}\right]\left(z_r\right)^N\left(z_v\right)^N\left(z_e\right)^N$$

Our goal is to calculate the thermodynamic properties of the ideal gas. These properties depend on the natural logarithm of the ideal-gas partition function. This is a sum of terms:

$$\ln Z_{IG} = \ln\left[\frac{\left(z_t\right)^N}{N!}\right] + N\ln z_r + N\ln z_v + N\ln z_e$$

In our development of classical thermodynamics, we find it convenient to express the properties of substance on a per-mole basis. For the same reasons, we focus on evaluating $\ln Z_{IG}$ for one mole of gas; that is, for the case that N is Avogadro's number, $\overline{N}$. We now examine the relationships that enable us to evaluate each of these contributions to $\ln Z_{IG}$.