

23.3: The Thermodynamic Functions of the N-molecule System

With the results of [Section 23.2](#) in hand, we can find the other thermodynamic functions for the N -molecule system from the equations for Z and \hat{P}_i by the arguments we use in Chapters 20 and 21. Let us summarize these arguments. From

$$E = \sum_{i=1}^{\infty} \hat{P}_i E_i$$

we have

$$dE = \sum_{i=1}^{\infty} E_i d\hat{P}_i + \sum_{i=1}^{\infty} \hat{P}_i dE_i$$

We associate the first term with dq^{rev} and the second term with $dw = -PdV$; that is,

$$dq^{rev} = TdS = \sum_{i=1}^{\infty} E_i d\hat{P}_i = -kT \sum_{i=1}^{\infty} \ln \left(\frac{\hat{P}_i}{\Omega_i} \right) d\hat{P}_i - kT \ln Z \sum_{i=1}^{\infty} d\hat{P}_i$$

Where we substitute

$$E_i = -kT \ln \left(\frac{\hat{P}_i}{\Omega_i} \right) - kT \ln Z$$

which we obtain by taking the natural logarithm of the partition function. Since $\sum_{i=1}^{\infty} d\hat{P}_i = 0$, we have for each system,

$$dS = -k \sum_{i=1}^{\infty} \ln \left(\frac{\hat{P}_i}{\Omega_i} \right) d\hat{P}_i = -k \sum_{i=1}^{\infty} \left\{ \Omega_i d \left(\frac{\hat{P}_i}{\Omega_i} \ln \frac{\hat{P}_i}{\Omega_i} \right) - d\hat{P}_i \right\} = -k \sum_{i=1}^{\infty} d \left(\hat{P}_i \ln \frac{\hat{P}_i}{\Omega_i} \right)$$

The system entropy, S , and the system-energy-level probabilities, \hat{P}_i , are functions of temperature. Integrating from $T = 0$ to T and choosing the lower limits for the integrations on the right to be $\hat{P}_1(0) = 1$ and $\hat{P}_i(0) = 0$ for $i > 1$, we have

$$\int_{S_0}^S dS = -k \sum_{i=1}^{\infty} \int_{\hat{P}_i(0)}^{\hat{P}_i(T)} d \left(\hat{P}_i \ln \frac{\hat{P}_i}{\Omega_i} \right)$$

Letting $\hat{P}_i(T) = \hat{P}_i$, the result is

$$\begin{aligned} S - S_0 &= -k \hat{P}_1 \ln \frac{\hat{P}_1}{\Omega_1} + k \ln \frac{1}{\Omega_1} - k \sum_{i=2}^{\infty} \hat{P}_i \ln \frac{\hat{P}_i}{\Omega_i} \\ &= -k \sum_{i=1}^{\infty} \hat{P}_i \ln \frac{\hat{P}_i}{\Omega_i} - k \ln \Omega_1 \end{aligned}$$

From the partition function, we have

$$\ln \left(\frac{\hat{P}_i}{\Omega_i} \right) = -\frac{E_i}{kT} + \ln Z$$

so that

$$\begin{aligned} S - S_0 &= -k \sum_{i=1}^{\infty} \hat{P}_i \left(-\frac{E_i}{kT} + \ln Z \right) - k \ln \Omega_1 \\ &= \frac{1}{T} \sum_{i=1}^{\infty} \hat{P}_i E_i + k \ln Z \sum_{i=1}^{\infty} \hat{P}_i - k \ln \Omega_1 \\ &= \frac{E}{T} + k \ln Z - k \ln \Omega_1 \end{aligned}$$

We take the system entropy at absolute zero, S_0 , to be

$$S_0 = k \ln \Omega_1$$

If the lowest energy state is non-degenerate, $\Omega_1 = 1$, and $S_0 = 0$, so that

$$S(T) = \frac{E}{T} + k \ln Z$$

As in [Section 21.6](#), we observe that

$$E = \sum_{i=1}^{\infty} \hat{P}_i E_i = Z^{-1} \sum_{i=1}^{\infty} \Omega_i E_i \exp\left(\frac{-E_i}{kT}\right)$$

and that

$$\left(\frac{\partial \ln Z}{\partial T}\right)_V = Z^{-1} \sum_{i=1}^{\infty} \Omega_i \left(\frac{E_i}{kT^2}\right) \exp\left(\frac{-E_i}{kT}\right) = \frac{E}{kT^2}$$

so that

$$E = kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V$$

From $A = E - TS$ and the entropy equation, $S = E/T + k \ln Z$, the Helmholtz free energy of the system is

$$A = -kT \ln Z$$

For the system pressure, we find from

$$P = -\left(\frac{\partial A}{\partial V}\right)_T$$

that

$$P = kT \left(\frac{\partial \ln Z}{\partial V}\right)_T$$

From $H = E + PV$, we find

$$H = kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V + V kT \left(\frac{\partial \ln Z}{\partial V}\right)_T$$

and from $G = E + PV - TS$, we find

$$G = V kT \left(\frac{\partial \ln Z}{\partial V}\right)_T - kT \ln Z$$

For the chemical potential per molecule in the N -molecule system, we obtain

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{VT} = -kT \left(\frac{\partial \ln Z}{\partial N}\right)_{VT}$$

Thus, we have found the principle thermodynamic functions for the N -molecule system expressed in terms of $\ln Z$ and its derivatives. The system partition function, Z , depends on the energy levels available to the N -molecule system. The thermodynamic functions we have obtained are valid for any system, including systems in which intermolecular forces make large contributions to the system energy. Of course, the system partition function, Z , must accurately reflect the effects of these forces.

In [Chapter 24](#) we find that the partition function, Z , for a system of N , distinguishable, non-interacting molecules is related in a simple way to the molecular partition function, z . We find $Z = z^N$. When we substitute this result for Z into the system partition functions developed above, we recover the same results that we developed in [Chapters 20](#) and [21](#) for the thermodynamic properties of a system of N , distinguishable, non-interacting molecules.

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