# 24.14: Problems

1. The partition function, $Z$, for a system of $N$, distinguishable, non-interacting molecules is $Z=z^N$, where $z$ is the molecular partition function, $z=\sum g_i \exp\left(-\epsilon_i/kT\right)$, and the $\epsilon_i$ and $g_i$ are the energy levels available to the molecule and their degeneracies. Show that the thermodynamic functions for the $N$-molecule system depend on the molecular partition function as follows:

(a) $E=NkT^2\left(\frac{\partial \ln z}{\partial T}\right)_V$

(b) $S=NkT\left(\frac{\partial \ln z}{\partial T}\right)_V+Nk\ln z$

(c) $A=-NkT\ln z$

(d) $P_{\text{system}}=NkT\left(\frac{\partial \ln z}{\partial V}\right)_T$

(e) $H=NkT^2\left(\frac{\partial \ln z}{\partial T}\right)_V+NkTV\left(\frac{\partial \ln z}{\partial V}\right)_T$

(f) $G=-NkT\ln z+NkTV\left(\frac{\partial \ln z}{\partial V}\right)_T$

2. When the number of available quantum states is much larger than the number of molecules, the partition function, $Z$, for a system of $N$, indistinguishable, non-interacting molecules is $Z=z^N/N!$, where $z$ is the molecular partition function, $z=\sum g_i \exp\left(-\epsilon_i/kT\right)$, and the $\epsilon_i$ and $g_i$ are the energy levels available to the molecule and their degeneracies. Show that the thermodynamic functions for the N-molecule system depend on the molecular partition function as follows:

(a) $E=NkT^2\left(\frac{\partial \ln z}{\partial T}\right)_V$

(b) $S=Nk\left[T\left(\frac{\partial \ln z}{\partial T}\right)_V+\ln\frac{z}{N}+1\right]$

(c) $A=-NkT\left[1+\ln\frac{z}{N}\right]$

(d) $P_{\text{system}}=NkT\left(\frac{\partial \ln z}{\partial V}\right)_T$

(e) $H=NkT^2\left(\frac{\partial \ln z}{\partial T}\right)_V+NkTV\left(\frac{\partial \ln z}{\partial V}\right)_T$

(f) $G=-NkT\left[1+\ln\frac{z}{N}+V\left(\frac{\partial \ln z}{\partial V}\right)_T\right]$

3. The molecular partition function for the translational motion of an ideal gas is

$$z_t=\left(\frac{2\pi mkT}{h^2}\right)^{3/2}V$$

The partition function for a gas of $N$, monatomic, ideal-gas molecules is $Z=z_t^N/N!$. Show that the thermodynamic functions are as follows:

(a) $E=\frac{3}{2}NkT$

(b) $S=Nk\left[\frac{5}{2}+\ln\frac{z}{N}\right]$

(c) $A=-NkT\left[1+\ln\frac{z}{N}\right]$

(d) $P_{\text{system}}=\frac{NkT}{V}$

(e) $H=\frac{5}{2}NkT$

(f) $G=-NkT\ln\frac{z}{N}$

4. Find $E$, $S$, $A$, $H$, and $G$ for one mole of Xenon at $300\text{ K}$ and $1$ bar.

**Notes**

[1] Data from the ***Handbook of Chemistry and Physics***, $79^{th}$ Ed., David R. Linde, Ed., CRC Press, New York, 1998.