

## 24.10: The Gibbs Free Energy for One Mole of An Ideal Gas

In our discussion of ensembles, we find that the thermodynamic functions for a system can be expressed as functions of the system's partition function. Now that we have found the molecular partition function for a diatomic ideal gas molecule, we can find the partition function,  $Z_{IG}$ , for a gas of  $N$  such molecules. From this system partition function, we can find all of the thermodynamic functions for this  $N$ -molecule ideal-gas system. The system entropy, energy, and partition function are related to each other by the equation

$$S = \frac{E}{T} + k \ln Z_{IG}$$

Rearranging, and adding  $(PV)_{\text{system}}$  to both sides, we find the Gibbs free energy

$$G = E - TS + (PV)_{\text{system}} = (PV)_{\text{system}} - kT \ln Z_{IG}$$

For a system of one mole of an ideal gas, we have  $(PV)_{\text{system}} = \bar{N}kT$ . If the ideal gas is diatomic, we can substitute the molecular partition functions developed above to find

$$\begin{aligned} G_{IG} &= \bar{N}kT - kT \ln Z_{IG} \\ &= \bar{N}kT - kT \ln \left[ \frac{(z_t)^{\bar{N}}}{\bar{N}!} \right] - \bar{N}kT \ln z_r - \bar{N}kT \ln z_v - \bar{N}kT \ln z_e \\ &= \bar{N}kT - \bar{N}kT - \bar{N}kT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT}{P} \right] - \bar{N}kT \ln \left( \frac{8\pi^2 IkT}{\sigma h^2} \right) - \bar{N}kT \ln \left( \frac{\exp(-h\nu/2kT)}{1 - \exp(-h\nu/kT)} \right) \\ &\quad - \bar{N}kT \ln \left( \frac{D_0}{RT} + \frac{h\nu}{2kT} \right) \end{aligned}$$

For the standard Gibbs free energy of an ideal gas, we define the pressure to be one bar. Introduction of this condition ( $P = P^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$ ) and further simplification gives

$$G_{IG}^\circ = -RT \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT}{P^\circ} \right] - RT \ln \left( \frac{8\pi^2 IkT}{\sigma h^2} \right) - RT \ln \left( \frac{\exp(-h\nu/2kT)}{1 - \exp(-h\nu/kT)} \right) - RT \left( \frac{D_0}{RT} + \frac{h\nu}{2kT} \right)$$

In this form, the successive terms represent, respectively, the translational, rotational, vibrational, and electronic contributions to the Gibbs free energy. Further simplification results because vibrational and electronic contributions from terms involving  $h\nu/2kT$  cancel. This is a computational convenience. Factoring out  $RT$ ,

$$G_{IG}^\circ = -RT \left\{ \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{kT}{P^\circ} \right] + \ln \left( \frac{8\pi^2 IkT}{\sigma h^2} \right) - \ln(1 - \exp(-h\nu/kT)) + \frac{D_0}{RT} \right\}$$

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