

24.13: The Reference State for Molecular Partition Functions

In Sections 24.11 and 24.12, we see that the standard Gibbs free energy, G° , that we calculate from our statistical thermodynamic model is not the same quantity as the Gibbs free energy of formation, $\Delta_f G^\circ$. Nevertheless, these calculations show that we can use the statistical-thermodynamic Gibbs free energies of the reacting species to calculate the Gibbs free energy change for a reaction in exactly the same way that we use the corresponding Gibbs free energies of formation.

The use of Gibbs free energies of formation for these calculations is successful because we measure all Gibbs free energies of formation relative to the Gibbs free energies of the constituent elements in their standard states. By convention, we set the standard-state Gibbs free energies of the elements equal to zero, but this is incidental; our method is successful because the Gibbs free energies of the constituent elements cancel out when we calculate the Gibbs free energy change for a reaction from the Gibbs free energies of formation of the reacting species.

Our statistical-mechanical Gibbs free energies represent the Gibbs free energy change for a different process. They correspond to the formation of the molecule from its isolated constituent atoms. The isolated constituent atoms are the reference state for our statistical-mechanical calculation of standard molar Gibbs free energies. We choose the Gibbs free energies of the isolated atoms to be zero. (Whatever Gibbs free energies we might assign to the isolated atoms, they cancel out when we calculate the Gibbs free energy change for a reaction from the statistical-thermodynamic Gibbs free energies of the reacting species.)

When we sum the component energies of our model for a diatomic molecule, we have

$$\epsilon_{\text{molecule}} = \epsilon_t + \epsilon_r + \epsilon_v + \epsilon_e.$$

The smallest of these quantum mechanically allowed values for $\epsilon_{\text{molecule}}$ is particularly significant in our present considerations. Once we have created this molecule in its lowest energy state, we can consider that we can get it into any other state just by adding energy to it. When the isolated constituent atoms are the reference state, the value of the lowest-energy state of the molecule is the energy exchanged with the surroundings when the molecule is formed in this state from the constituent atoms.

Reviewing our models for the motions that a diatomic molecule can undergo, we see that the translational and rotational energies can be zero. The smallest vibrational energy is $h\nu/2$, and the smallest electronic energy is

$$-\left(\frac{D_0}{N} + \frac{h\nu}{2}\right)$$

The minimum molecular energy is $\epsilon_{\text{molecule}}^{\text{minimum}} = -D_0/\bar{N} < 0$. Since D_0/\bar{N} is the energy required to just separate the diatomic molecule into its constituent elements, the end product of this process is two stationary atoms, situated at an infinite distance from one another. Conversely, $\epsilon_{\text{molecule}}^{\text{minimum}}$ is the energy released when the stationary constituent atoms approach one another from infinite separation to form the diatomic molecule in its lowest energy state. The reference state for the statistical-mechanical calculation of molecular thermodynamic properties is a set of isolated constituent atoms that have no kinetic energy. The stipulation that the reference-state atoms have no kinetic energy is often expressed by saying that the reference state is the constituent atoms at the absolute zero of temperature.

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