ChemActivity **18**

# Thermal Energies

(What is temperature?)

We have seen that the energy of a molecule can be separated into translational, rotational, vibrational, and electronic energies. Within each type of energy, the energy levels are quantized. Each energy state is described by a wave function which depends on a quantum number or a set of quantum numbers. For example, a particular molecule of dihydrogen, $H_2$, in a box could be described as follows:

translational: $n_x = 4.12 \times 10^7$ , $n_y = 8.22 \times 10^2$ , $n_z = 4.37 \times 10^{11}$
rotational: $J = 12$ , $m = 5$
vibrational: $\upsilon = 0$
electronic: $^1\Sigma_g$ or $(\sigma_g^2)$ the electronic ground state

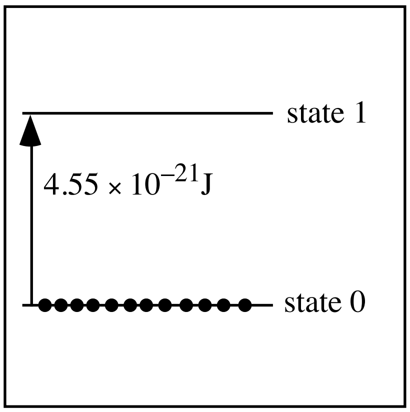
This molecule is in the ground electronic state. The two electrons are paired in a gerade bonding orbital. The molecule has no spin angular momentum. The molecule has no orbital angular momentum. The molecule is in the lowest possible vibrational energy state. The molecule has a modest amount of rotational energy. The molecule is moving fastest in the *z* direction and slowest in the *y* direction.

We now turn our attention to how a collection of molecules is distributed throughout the available energy states.

## Model 1: A Hypothetical Molecule with only Two States at Different Energy Levels.

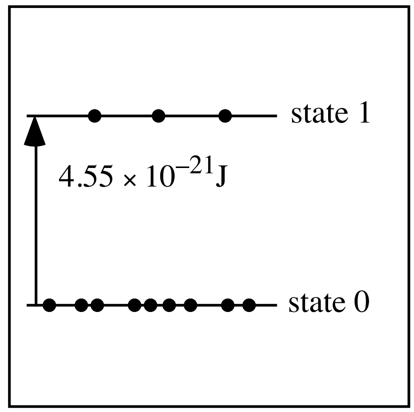
● = molecule

$T = 0$ K



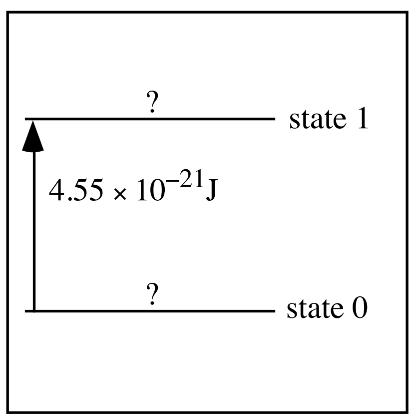

All of the molecules are in the lowest possible energy level at $T = 0$ K.

$T = 300$ K




As the temperature increases, some of the molecules gain energy. One-fourth of the molecules are in the excited state at $T = 300$ K

$T = \infty$ K




## Information

The thermal energy is defined as the energy that the system has because it is at some temperature other than zero K.

## Critical Thinking Questions

1. Why is state 1 not populated at $T = 0$ K?

2. Why does state 1 become populated at a temperature greater than $T = 0$ K?

3. Predict the number of molecules in state 0 and in state 1 at $T = \infty$ K.

4. What is the thermal energy for the twelve molecules in Model 1 at $T = 0$ K?

5. What is the thermal energy for the twelve molecules in Model 1 at $T = 300$ K?

6. What is the thermal energy per molecule in Model 1 at $T = 300$ K?

7. What is the thermal energy per mole in Model 1 at $T = 300$ K?

## Model 2: The Boltzmann Distribution.

Ludwig Boltzmann developed an equation that yields the ratio of the number of molecules at two different energy levels, *i* and *j*, when the molecules are in thermal equilibrium. The equation is known as the Boltzmann distribution equation.

$$\frac{N_i}{N_j} = \frac{g_i}{g_j}\, e^{-(\varepsilon_i - \varepsilon_j)/kT} \qquad (1)$$

where

$\varepsilon_i$ and $\varepsilon_j$ are the energies associated with the two energy levels

$g_i$ and $g_j$ are the degeneracies of the i and j energy levels, respectively

$k$ is Boltzmann's constant, $1.380 \times 10^{-23}$ J/K

$T$ is the temperature in K

## Critical Thinking Questions

8. Use Boltzmann's equation to verify that all of the molecules will be found in state 0 at $T$ = 0 K (Model 1). [Hint: determine the ratio $N_1/N_0$.]

9. Use Boltzmann's equation to verify that three molecules of twelve will be found in state 1 at $T$ = 300 K (Model 1).

10. Use Boltzmann's equation to determine the number of molecules in state 1 at $T = \infty$ K (Model 1).

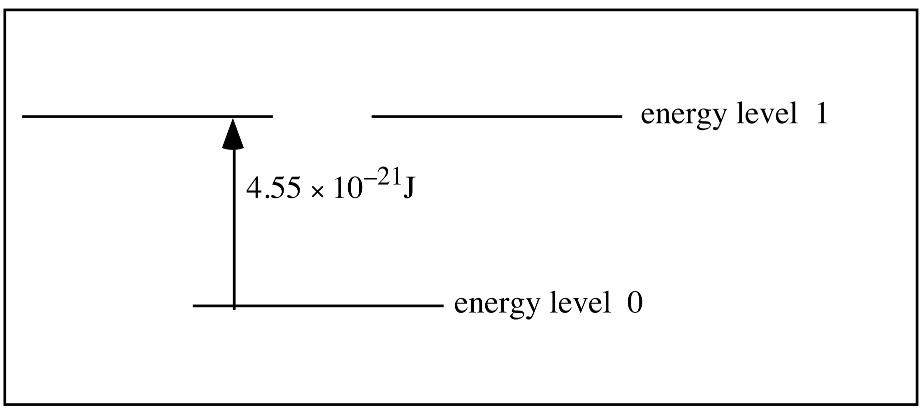
11. Compare your prediction (CTQ 3) to the result obtained from the Boltzmann distribution equation.

## Information

At infinite temperature there is sufficient energy available such that the molecules will simply populate all energy states without regard to energy. If there are 10 states, all will be equally occupied at $T = \infty$ K.

## Exercises

1. For one mole of molecules, find the number of molecules in state 0 and state 1 at $T = 0$, 300, and $\infty$ K for the following system. Note that energy level 1 is two-fold degenerate.




2. A system has three energy levels: $\varepsilon_0$, $\varepsilon_1$, and $\varepsilon_2$. The degeneracies of these energy levels are as follows: $g_0 = 2$; $g_1 = 1$; $g_2 = 9$. If one mole of molecules are placed into the system at $T = \infty$ and allowed to come to thermal equilibrium, how many molecules will be found in the $\varepsilon_0$ energy level?

## Model 3: The Partition Function.

$$U_{\text{thermal}} = \frac{N}{q}\, kT^2 \frac{dq}{dT} \qquad (2)$$

where:

$N$ is the total number of molecules

$$q = \sum_{i=0}^{i_{max}} g_i \, e^{-(\varepsilon_i - \varepsilon_o)/kT} \qquad (3)$$

$q$ is called the **partition function**

## Critical Thinking Questions

12. Show that the partition function for the system in Model 1 is

$$q = 1 + e^{-(330)/T}$$

13. Show that $\dfrac{dq}{dT} = \dfrac{330}{T^2} \, \mathrm{e}^{-(330)/T}$

14. Evaluate $q$ and $dq/dT$ at 300 K. Use the equation for the thermal energy, equation (2) to calculate the thermal energy for 12 molecules at 300 K (Model 1). How does your value compare to the value calculated in CTQ 5?

## Exercise

3. Find the thermal energy of one mole of molecules described by the system in Exercise 1 at 300 K. Explain in words why one mole of molecules described by the system in Exercise 1 has more thermal energy than one of molecules described by Model 1.