Temperature as a Measure of the Distribution of Particles Over Energy States: Would a Negative Absolute Temperature be Very Cold, or Very Hot?

by

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Abstract

This exercise explores the implications of the Boltzmann Equation for the population of energy states as a function of temperature. It uses the graphing power of Mathcad to provide a concrete, visual presentation of relative population of the first four vibrational states of carbon monoxide from 0 K to very high temperatures and focuses attention on what happens to the relative populations of these states over that range, especially at the extremes of infinite and zero absolute temperature. It then seeks to increase the user's understanding of the Boltzmann Equation by exploring the implications of hypothetical negative absolute temperatures and asking the question "Would negative absolute temperature be very hot or very cold?"

Goal

The goal of this exercise is to enhance the user's knowledge and understanding of

1. the relationships of the populations of different energy states of a system to each other and to temperature;

2. these relationships as the physical implications of the Boltzmann Equation.

Performance Objectives

After completing this exercise the user should be able to

1. Discuss the relationship between the populations of one or more excited states and the ground state and among the populations of the excited states themselves, including sketching a graph of the populations of the excited states vs. temperature.

2. Give specific values for the ratio of the population of an excited state to the population of the ground state at zero and infinite absolute temperature.

3. Calculate the percentage of atoms or molecules in a given state given the temperature and the energies of the states of the system.

4. Discuss the "hotness" of negative absolute temperatures in terms of the relationship of the populations of excited states to that of the ground state.

References and Suggestions for Further Reading

1. Atkins, Peter; de Paula, Julio *Physical Chemistry*, 7th ed.; W.H. Freeman: New York, 2002; Sections 19.1 and 19.2

2. Laidler, Keith J.; Meiser, John H.; Sanctuary, Bryan C. *Physical Chemistry*, 4th ed.; Houghton Mifflin: Boston, 2003; Section 15.2

3. Ball, David W. *Physical Chemistry;* Brooks/Cole: Pacific Grove, CA, 2003; Sections 17.1-17.4

4. McDowell, Sean A.C. *J. Chem. Educ.* **1999,** 76, 1393-1394

Introduction

Of the various ways of defining temperature, perhaps the most sophisticated, and at the same time the most fundamental, is that it is the property that determines the distribution of the particles of a system (atoms, molecules, etc.) over the energy levels available to them when the system is at equilibrium. This distribution is expressed through the **Boltzmann Equation,** which, if we ignore energy state degeneracy, can be expressed (See Ref. 1) by

$$N_i = \frac{N_{tot} \cdot e^{\frac{-\left(E_i - E_0\right)}{k \cdot T}}}{\sum_j e^{\frac{-\left(E_j - E_0\right)}{k \cdot T}}}$$

where N_{tot} is the total number of particles in the system, N_i is the number of particles in the ith energy state, E_i is the energy of the ith state, E_0 is the energy of the ground or lowest energy state, k is the Boltzmann constant, and T is the absolute temperature in Kelvin. The summation in the denominator is taken over all of the energy levels of the system.

In this exercise we will look at how N_i and the relationship between N_i and N_0 change with temperature and will ask ourselves the interesting question of whether a negative absolute temperature, if it existed, should be considered very cold or very hot. We will do this in the context of a system that has four possible energy levels. We will start with the values of some quantities already assigned. N_{tot} is arbitrarily assigned a value of 1 X 10^6. Values are also assigned for the four energy levels, E_0 through E_3. For the purpose of this exercise it is not necessary that the assigned energies correspond to any real system, but in fact they were chosen to be the energies of the first four vibrational energy levels of the CO molecule in the harmonic oscillator approximation.

Assignment of Parameters

$N_{tot} := 1 \cdot 10^{6}$ $k := 1.38066 \cdot 10^{-23} \cdot \frac{J}{K}$ $i := 0, 1 .. 3$ $j := 0, 1 .. 3$

$E_0 := 2.129 \cdot 10^{-20} \cdot J$ $E_1 := 6.386 \cdot 10^{-20} \cdot J$ $E_2 := 1.064 \cdot 10^{-19} \cdot J$ $E_3 := 1.490 \cdot 10^{-19} \cdot J$

The Boltzmann Equation tells us that the number of molecules in the ith state (i = 0, 1, 2, or 3) at temperature T is

$$N(i, T) := \frac{N_{tot} \cdot e^{\frac{-(E_i - E_0)}{k \cdot T}}}{\sum_j e^{\frac{-(E_j - E_0)}{k \cdot T}}} \qquad T := 0, 100 .. 2 \times 10^{5}$$

Exercise 1

Using the **Enter** key clear some space below this text box. (Click on any text in this box to see the outlines of the box and where it ends.) Then set up a two-dimensional graph (use the @ key or select X-Y plot from the Graph palette on the Math toolbar). Use this graph to plot the number of molecules in the four energy states as a function of temperature by inserting **T** as the x-axis variable and **N(0,T), N(1,T), N(2,T), and N(3,T)** as the y-axis variables.

Answer each of the questions in this exercise in the space below the text box containing the question. Use the Enter key to clear space for your answer.

a. What happens to N_0, N_1, N_2, and N_3, both absolute terms and in relation to each other as the temperature, T, rises? What happens when the temperature gets very high?
The results you have seen here will apply to the ground and excited states of any system regardless of their energies, if the temperature gets high enough. After you finish Exercise 3 you can demonstrate this for yourself by changing the assigned energies and playing with the upper limit of x in the graph.

b. What conclusion can you draw about the population distribution of the energy states of a system as T approaches infinity?

c. As the temperature rises from 0 K is there any point at which N_1, N_2, or N_3 becomes greater than N_0? Can you explain your answer in terms of the form of the Boltzmann Equation?

d. What do you see happening to N_0, N_1, N_2, and N_3 as the temperature, T, approaches 0?

Again, the results you have seen here will apply to the ground and excited states of any system regardless of their energies

e. What conclusion can you draw about the population distribution of the energy states of a system at T = 0?

Exercise 2

$$T := -1\cdot 10^{5}, -9.99\cdot 10^{4} .. 2\cdot 10^{5}$$

Now let us look at the physically impossible but nonetheless imaginable situation of negative absolute temperature. Above T has been redefined with a range from -1 X 10^5 K to + 2 X 10^5 K. Below this text box use the Enter key to create space for a graph and then create it by using the @ key or selecting X-Y plot from the Graph palette on the Math toolbar. Plot **T** as the x-axis variable and **N(0,T)** and **N(3,T)** as y-axis variables. If necessary, redefine the lower limit on the x axis as -1 X 10^5 to bring the curves all the way to the left edge of the graph.

f. If you think about the relationship between N_0 and N_3 at negative absolute temperatures in terms of the trend in the relationship between them as temperature approaches +∞, would you say that negative absolute temperatures are very hot or very cold. Explain your reasoning.

What you see happening to the relationship between N_3 and N_0 at negative temperatures corresponds to what is called a "population inversion".

g. Can you think of a kind of device with many uses in today's society whose operation depends on population inversions?

Exercise 3

$$T := 0, 10 .. 300$$

Now let us look at the populations of the excited state N_1, N_2, and N_3, at temperatures around or below room temperature. For this purpose T has been redefined to be in the range from 0 to 300 K, a value close to room temperature. Copy your graph from Exercise 1 into the space below this text box, using the Enter key to clear space for it. Delete N(0,T) from the y axis.

h. Estimate what percentage of the molecules are in the first excited (E_1) state 300 K.

(Remember what the total number of molecule in the system is.)

i. What does your graph tell you about the values of N_2 and N_3 at 300 K?

j. From the values of N_1, N_2, and N_3 what conclusion can you draw about the fraction of CO molecules that will be in excited vibrational states at 300 K? Explain your answer.