Heat, Work and Entropy: A Molecular Level Illustration

Dr. Jeffrey A. Draves
Monmouth College
Department of Chemistry
700 E. Broadway
Monmouth, Il 61462
jeffd@monm.edu

Abstract

This worksheet is intended to help students understand the difference between heat and work at the molecular level and to appreciate the use of the term (dis)order when applied to entropy. The worksheet makes use of quantum mechanics, statistical mechanics and classical thermodynamics to illustrate these differences. The worksheet is simple to execute and has been tested in both Mathcad versions 6 and 2000. Questions and Exercises are placed throughout the worksheet which help guide students and draw connections between concepts.

Place in the Curriculum

The author has found that the illustration is best appreciated after classical thermodynamics, quantum mechanics and statistical mechanics have been introduced. However, the worksheet can be used at several other places in the Physical Chemistry curriculum but students have great difficulty in understanding the implications of the particle-in-a-box if background material is not provided.

The material in black are solutions, material in blue are general notes and suggestions for students, and the material in red are questions and exercises for the students to complete. When used as a review, all of the material in black is removed from the student version (unless otherwise noted).

Introduction

The distinction between heat and work and the concept of entropy are not easily grasped. Heat is often presented as energy transfer making use of disordered molecular motion while work is the transfer of energy which makes use of orderly molecular motion.[1] Entropy is often described by analogy with macroscopic (dis)order of matter, an approach which has recently been called the "cracked crutch."[2] Analogies that equate entropy change to molecular (dis)order and describe heat and work as transfer through (dis)orderly motion further complicate the understanding of these three quantities.

To gain a conceptual understanding of these quantities and their relationship on a molecular level, knowledge of the Boltzmann distribution, quantum mechanics and thermodynamics is required and even then, an illustration of the relationship can be tedious if done by hand. Fortunately, the development of software packages like Mathcad have allowed this illustration to be achieved effectively while removing the tedium.

Goals

There are three major goals of this worksheet. They are:

to provide students with an understanding of the difference between heat and work and to refine and focus the use of the term "order" on the population distribution in a system,

to show students how heat, work, and entropy manifest themselves at the molecular level, and

to provide an illustration of how thermodynamics, quantum mechanics and statistical mechanics can be brought to bear on a problem to improve one's understanding.

Objectives

Upon completion of this worksheet, students should be able to:

calculate and compare the classical and statistical methods for determining the changes in energy and entropy of a model system during constant-volume heating and adiabatic compression,

calculate the partition function before and after a system is subjected to constant-volume heating and to adiabatic compression and compare the results,

relate the values of the partition functions to entropy and to (dis)order,

produce bar charts of state populations and relate these to entropy and (dis)order for constant-volume heating and adiabatic compression and compare the results, and

properly apply the term (dis)order when discussing entropy.

Background Preparation for Students

Students should review the following material in their physical chemistry textbook. References 1, 3 and 4 provide solid background for this material.

<u>Classical Thermodynamics</u>: Review the concepts of heat, work and entropy and be able to calculate the internal energy change of a closed system, containing an ideal gas when the system is heated (Experiment 1) and when the system has work done on it reversibly and adiabatically (Experiment 2). Also be able to calculate the entropy change for the system.

<u>Quantum Mechanical Particle-in-a-Box:</u> Review the concepts of a particle-in-a-box and be able to calculate the energy levels for a 1 dimensional box.

<u>Statistical Mechanics:</u> Review the information regarding the partition function and be able to evaluate the partition function using the energy levels for a particle-in-a-box.

<u>Boltzmann Law:</u> Review the Boltzmann Law and be able to evaluate the population of energy levels for a particle-in-a-box.

Worksheet

The worksheet is divided into four sections. These are **Section I: The Experiments, Section II: Molecular Energy Levels, Section III:The Effect of a Volume Change on the Particle in a Box Energy Levels,** and **Section IV: Summary**

The system you are to consider contains 1 mole of He atoms, assumed to behave ideally, confined to a cubic box with dimensions of 0.3 m on each side. The Initial system temperature is 273 Kelvin. You will conduct two experiments and analyze the results. The first experiment will determine the change in internal energy when the system is heated to 323 Kelvin at constant volume with no additional work possible. The second experiment will produce the same change in internal energy by doing work on the system, reversibly and adiabatically.

You will use the results of these two experiments to investigate what effects the method for changing the internal energy has on the system at the molecular level. You will also examine the entropy changes these systems undergo during the experiments.

Section I: The Experiments

Some useful constants [given to students]

$h := 6.62608\cdot 10^{-34}\cdot joule\cdot sec$ $\quad N_A := \frac{6.02214\cdot 10^{23}}{mole}$

$k_b := 1.38066\cdot 10^{-23}\cdot \frac{joule}{K}$ $\quad R := 8.31451\cdot \frac{joule}{K\cdot mole}$

To assign a value or insert an expression you must use the " shift ;" key (Mathcad will display :=) **not** the regular equal sign. The regular equal sign is reserved for evaluating a quantity.

Experiment 1
Consider a system of 1.00 mole of He atoms confined to a cubic box with sides of 0.300 meters in length and whose temperature is initially 273K. Determine the change in internal energy of the system if the temperature of the system is raised to 323K keeping the volume constant and allowing no additional work to be done.

Solution

$T_i := 273 \cdot K$ $\quad$ $T_f := 323 \cdot K$

$C_{v.m} := 12.47 \cdot \frac{joule}{K \cdot mole}$ $\quad$ $C_v := \frac{C_{v.m}}{N_A}$

The subscripts used in the quantities at the left are labels. They are inserted by using the " [" key. The labels "i" and "f" refer to the initial and final states respectively, "m" refers to a molar quantity, and "V" indicates volume.

The internal energy change in the absence of any pV or additional work is given by $\Delta U := N_A \cdot C_v \cdot (T_f - T_i)$ where i and f refer to the initial and final states, respectively

$$\Delta U := N_A \cdot C_v \cdot (T_f - T_i)$$

$$\Delta U = 623.5 \frac{joule}{mole}$$

It is not necessary to evaluate ΔU but doing so will provide a check of your work. Remember that you will need to type in "joule" or just be satisfied with the base units Mathcad gives you.

Experiment 2
Using the same system as in **Experiment 1** and your calculated change in internal energy from **Experiment 1**, find the volume to which the system must be compressed to achieve the same change in internal energy. Assume the process is reversible and adiabatic. Determine the amount of work done on the system. What is the final temperature of the system?

Solution

$L_i := 0.3 \cdot m$ $\quad$ $V_i := (L_i)^3$ $\quad$ $V_i = 0.027 m^3$

To evaluate a quantity in Mathcad you'll need to use the regular equal sign on the key board. It is not necessary to evaluate the quantities on the left, but doing so will provide a check on the work!

Given that we have an ideal gas and the work is done reversibly and adiabatically, the change in internal energy is equivalent to the work. So we are asking the question "To what volume would we need to compress the system to get to the same final temperature of 323K given an initial temperature of 273K?"

The final volume is obtained by using $V_f := V_i \cdot \left(\frac{T_f}{T_i}\right)^{\frac{-C_{v.m}}{R}}$.

$$V_f := V_i \cdot \left(\frac{T_f}{T_i}\right)^{\frac{-C_{v.m}}{R}} \qquad V_f = 0.021\,m^3$$

To evaluate a quantity in Mathcad you'll need to use the regular equal sign on the key board. It is not necessary to evaluate the quantities on the left, but doing so will provide a check on the work!

$$L_f := \sqrt[3]{V_f} \qquad L_f = 0.276\,m$$

Question 1. Explain why the final temperature in each of the experiments is the same? Would this be true if we had a real gas?

Exercise 1. Calculate the classical entropy change of the system for each of these experiments. Which of the final states, heat or work, is most disordered Justify your answer using the final macroscopic properties (p,V,T) of the system.

Section II: Molecular Energy Levels

For simplicity, the 1D Particle-in-a-Box (instead of the 3D) will be used to model the quantum mechanical nature of the system.

Calculate the zero point energy for the final state of Experiment 1, referred to as "Final-Heat," and the final state of Experiment 2, referred to as "Final-Work."

Needed Information [given to students] $MM := 4.00 \cdot \frac{g}{mole}$ $mass := \frac{MM}{1000 \cdot \frac{g}{kg} \cdot N_A}$

Solution

$EHeat_0 := \frac{h^2}{8 \cdot mass \cdot L_i^2}$ $EHeat_0 = 9.181 \times 10^{-41}$ joule

$EWork_0 := \frac{h^2}{8 \cdot mass \cdot L_f^2}$ $EWork_0 = 1.086 \times 10^{-40}$ joule

Calculate the energy for the values of n given below relative to the zero point energy. To see why these values were chosen scroll to the column on the right. The label "j" is used for indexing the energy states and "n" represents the quantum number.

$I := 10$

$j := 0 .. I - 1$

$n_j :=$

1
10^3
10^4
10^5
10^6
10^7
10^8
10^9
10^{10}
10^{11}

"j" is an index, not a label. It is inserted into a MathCad document by using the "[" key.

To determine a suitable range for calculating energy levels you first need to get a feel for the size of n (n1 is used here to avoid confusion in the worksheet) near the temperatures of the experiments, use 300K. To do so, set the energy expression for the particle in a 1-D box equal to the thermal energy of $k_B T$ and solve for n1.

Note that the equal sign from the Boolean pallet should be used here.

Solution

$$T := 300 \cdot K \qquad \frac{n1^2 \cdot h^2}{8 \cdot mass \cdot L_f} = k_b \cdot T$$

Solving for n1 using the Sybolics-variable-solve command with the cursor behind n1 gives:

$$\begin{bmatrix} 2 \cdot 2^{\frac{1}{2}} \cdot \dfrac{\left(k_b \cdot T \cdot mass \cdot L_f\right)^{\frac{1}{2}}}{h} \\ -2 \cdot 2^{\frac{1}{2}} \cdot \dfrac{\left(k_b \cdot T \cdot mass \cdot L_f\right)^{\frac{1}{2}}}{h} \end{bmatrix}$$

Taking the positive root and equating it to n1 gives:

$$n1 := 2 \cdot 2^{\frac{1}{2}} \cdot \frac{\left(k_b \cdot T \cdot mass \cdot L_f^{\,2}\right)^{\frac{1}{2}}}{h}$$

$$n1 = 6.175 \times 10^9$$

$EHeat(n) := (n)^2 \cdot EHeat_0 - EHeat_0$ $EWork(n) := (n)^2 \cdot EWork_0 - EWork_0$

$EHeat(n) =$

0
$9.181 \cdot 10^{-35}$
$9.181 \cdot 10^{-33}$
$9.181 \cdot 10^{-31}$
$9.181 \cdot 10^{-29}$
$9.181 \cdot 10^{-27}$
$9.181 \cdot 10^{-25}$
$9.181 \cdot 10^{-23}$
$9.181 \cdot 10^{-21}$
$9.181 \cdot 10^{-19}$

joule

$EWork(n) =$

0
$1.086 \cdot 10^{-34}$
$1.086 \cdot 10^{-32}$
$1.086 \cdot 10^{-30}$
$1.086 \cdot 10^{-28}$
$1.086 \cdot 10^{-26}$
$1.086 \cdot 10^{-24}$
$1.086 \cdot 10^{-22}$
$1.086 \cdot 10^{-20}$
$1.086 \cdot 10^{-18}$

joule

When one evaluates a quantity which has been indexed, all of the values appear.

Question 2. The energy levels of the initial system are identical to those of the Final-Heat system (Experiment I), but not of the Final-Work system (Experiment 2). Calculate the energy levels of the initial system to verify this. Explain why there is a change in energy levels for Experiment 2 but not for Experiment 1.

Question 3 Compare and offer an explanation for any differences in the energy levels for the Initial, Final-Heat, and Final-Work states.

Section III, Part A: The Effect of Volume Change on the Particle in a Box Energy Levels-A Numerical Representation

We will now connect the macroscopic thermodynamic results with the molecular level quantum mechanical results using statistical mechanics.

Evaluate the partition function for the Initial state, the Final-Heat state, and the Final-Work state of the system.

Solution

Here, it is important to evaluate the partition functions!

$$qInitial := \frac{V_i}{\left(\frac{h^2}{2\cdot\pi\cdot mass\cdot k_b\cdot T_i}\right)^{1.5}}$$

$$qInitial = 1.831 \times 10^{29}$$

$$qHeat := \frac{V_i}{\left(\frac{h^2}{2\cdot\pi\cdot mass\cdot k_b\cdot T_f}\right)^{1.5}}$$

$$qHeat = 2.356 \times 10^{29}$$

$$qWork := \frac{V_f}{\left(\frac{h^2}{2\cdot\pi\cdot mass\cdot k_b\cdot T_f}\right)^{1.5}}$$

$$qWork = 1.831 \times 10^{29}$$

Question 4a. What does the partition function tell us about the accessibility of states?
Question 4b. What does a value of q=1 tell us about the accessible number of energy states?
Question 5a. Compare the values for each of the partition functions and comment on their similarities and differences. What do the values you calculated for qInitial, qWork, and qHeat imply about molecular level (dis)order?
Question 5b. What does the value q=1 imply about molecular level (dis)order?

Exercise 2. Calculate the statistical entropy for the Initial state, the Final-Heat state, the Final-Work state, and for a system in which q=1. Calculate the change in entropy from the initial state to each of the final states.

Question 6. Compare the entropy values you calculated in Exercise 2 to each other and to those that were calculated in Exercise 1.

Question 7. Compare the entropy values to the values of the partition functions. What relationship exists between the value of the partition function and the entropy? What does this imply about the available number of states and the (dis)order of the system?

Section III, Part B: The Effect of Volume Change on the Particle in a Box Energy Levels-A Graphical Representation

Calculate the population of each of the ten energy levels given above for the Initial, Final-Heat, and Final-Work states.

Solution

$$N := 1 \cdot mole \cdot N_A$$

$$pInitial(n) := \frac{N \cdot \exp\left(-\frac{EHeat(n)}{k_b \cdot T_i}\right)}{qInitial}$$

Here, it is important to evaluate the population of each state!

$$pHeatfinal(n) := \frac{N \cdot \exp\left(-\frac{EHeat(n)}{k_b \cdot T_f}\right)}{qHeat}$$

$$pWorkfinal(n) := \frac{N \cdot \exp\left(-\frac{EWork(n)}{k_b \cdot T_f}\right)}{qWork}$$

pInitial(n) =	pHeatfinal(n) =	pWorkfinal(n) =
$3.289 \cdot 10^{-6}$	$2.556 \cdot 10^{-6}$	$3.289 \cdot 10^{-6}$
$3.289 \cdot 10^{-6}$	$2.556 \cdot 10^{-6}$	$3.289 \cdot 10^{-6}$
$3.289 \cdot 10^{-6}$	$2.556 \cdot 10^{-6}$	$3.289 \cdot 10^{-6}$
$3.289 \cdot 10^{-6}$	$2.556 \cdot 10^{-6}$	$3.289 \cdot 10^{-6}$
$3.289 \cdot 10^{-6}$	$2.556 \cdot 10^{-6}$	$3.289 \cdot 10^{-6}$
$3.289 \cdot 10^{-6}$	$2.556 \cdot 10^{-6}$	$3.289 \cdot 10^{-6}$
$3.288 \cdot 10^{-6}$	$2.555 \cdot 10^{-6}$	$3.288 \cdot 10^{-6}$
$3.21 \cdot 10^{-6}$	$2.504 \cdot 10^{-6}$	$3.21 \cdot 10^{-6}$
$2.879 \cdot 10^{-7}$	$3.262 \cdot 10^{-7}$	$2.879 \cdot 10^{-7}$
$5.449 \cdot 10^{-112}$	$1.003 \cdot 10^{-95}$	$5.48 \cdot 10^{-112}$

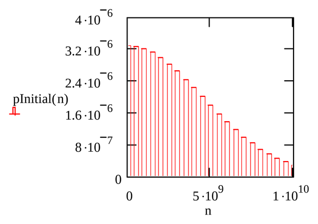
Question 8. Compare the populations of the three systems and comment on their similarities and differences.

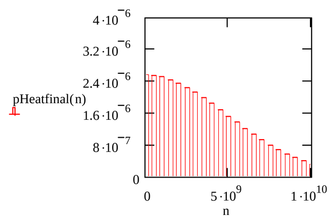
Produce a bar chart for the population of the states for the Initial, Final-Heat, and Final-Work states.

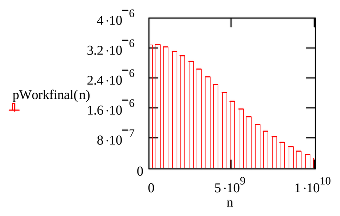
Solution To make a bar chart you must first produce the usual line plot then double click on the plot, select the "Traces" tab, and under "type" select "bar."

$n := 1, 5\cdot10^{8} .. 1\cdot10^{10}$

Be sure that each of the bar charts has the same scale. To do this click on the bar chart and type the upper scale limit into the black box. It might also be useful to increase the number of grids on the y-axis. To do this, double click on the chart and change the grid spacing in the y-axis box.







Exercise 3. Determine the value of q and produce a bar chart of the population distribution when T=0K (Note, Mathcad won't like T=0K so just use a very small number like 10^{-10}K.)

Question 9. When examining the population distribution bar charts, what similarities and differences do you observe when you compare the Final-Heat state to the Initial state? The Final-Heat state to the Final-Work state? The Final-Work state to the Initial state? What can you say about the T=0K population distribution bar chart?

Question 10. What characteristics of the bar charts represent a highly ordered system? A more disordered system?

Question 11. The total energy change of Experiments 1 and 2 was identical. What molecular level changes occurred to accommodate the energy change when a) the system underwent constant-volume heating? b) work was done on the system?

Question 12. Review your answers to Exercise 2 (along with questions 6 and 7) and to Exercise 3 (along with questions 9 and 10). For which means of energy change, heat or work, did:
a. the entropy change the most? the least?
b. the partition function change the most? the least?
c. the population distribution bar charts change the most? the least?

Question 13. When the entropy of the system changed, what changes could be observed in the population distribution bar charts? What changes could be observed in the value of the partition function? What do these changes imply about disorder?

Question 14. Write a summary of the effects energy change has on the population distribution in each of the experiments and offer a molecular level explanation of why one means of changing the internal energy is accompanied by a change in system entropy while the other means of changing internal energy results in no change in the entropy. How might these changes be explained using the term (dis)order?

References

1. P. Atkins and J. dePaula, *Physical Chemistry*, 7th Ed., W. H. Freeman and Company, New York, NY., 2002.

2. F. L. Lambert, *Disorder-A Cracked Crutch for Supporting Entropy Discussions*, J. Chem. Ed., 2002, 79, 187.

3. J. H. Noggle, *Physical Chemistry*, 3rd Ed. HapperCollins College Publishers, New York, NY., 1996.

4. R. G. Mortimer, *Physical Chemistry*, 2nd Ed., Academic Press, San Diego, CA., 2000.