Mathematica Observations

Introduction

Mathematica is a powerful programming language that simplifies many types of mathematical calculations and manipulations. It provides an environment for solving equations, differentiating equations, visualizing solutions in two and three dimensions, and even animating solutions. In this laboratory, you work through examples from physical chemistry and gain a sense of the possibilities with Mathematica.

Procedure

As with many powerful programs, the challenge to using Mathematica is to overcome the barrier to entry, and access the features of the program. Mathematica is a huge consumer of computer time, so you may have to be patient while, for example, three-dimensional animations are rendered. It is important to allocate as much memory to Mathematica as your computer can handle. The suggested size is 13312 K; Thoman suggests four times that much. A key-served version of Mathematica (version 4 or 5) is available at Williams. This should already be loaded on most of the computers in the physical chemistry lab (253 MSL) and in the molecular modeling lab (210 TCL).

Older versions of Mathematica are tedious to open. You need to start the program and start the "kernel", which is the portion of the program that does the intense mathematical work. In older installations, the kernel might run on another computer. Thankfully, in Mathematica 4.1 and later, you can start the program by double clicking on the file "MATH_366.STUD.nb" or any other Mathematica file. The "nb" extension stands for "notebook", which is a folder-like object in Mathematica. When you open the notebook, you'll see a series of brackets on the right-hand side, which correspond to paragraph-like objects. Click to place the cursor at the right end of a line (say the first line, **5 + 7**), then hit the enter key, and watch how Mathematica proceeds. Note that the return key will not work, but that Shift-Return will work like the enter key.

Work through the entire notebook, and save the notebook with the name "YOURLASTNAME_1.nb". Close your notebook when you are finished.

There are several steps that may frustrate or annoy you. Mathematica warns you when you define variables with names that are too similar, and the computer will beep. Ignore these warnings. You will get a confusing error message if you have not previously defined a variable. To remedy this situation, go back in the notebook and be sure that you have "entered" all of the definitions.

Safety considerations:

While you need not wear goggles while working at the computer, it is essential that you have goggles with you in the lab at all times. If you leave the computer work area for any reason, you need to be wearing goggles. Your colleagues will be doing experiments with the danger of broken glass and/or solvent spills, and your eyes are worth protecting.

Report

There is no formal report for this lab. In the CHEM 366 folder on the laboratory computer, save the notebooks that you produce.

Using Mathematica, please try to answer following questions:

Problem 1 How many possible arrangements are there for a pack of 52 cards?

Problem 2 The heat capacity of lead varies with temperature as follows:

T/K	C_P /JK^{-1} mol^{-1}
10	2.8
15	7.0
20	10.8
25	14.1
30	16.5
50	21.4
70	23.3
100	24.5
150	25.3
200	25.8
250	26.2
298	26.6

Calculate the standard Third Law entropy of lead at a) 0°C and b) 25°C.
You'll need to do some curve fitting to find the heat capacity as a function of temperature, and then integrate this function to obtain the entropy. Try some polynomial-type fits and make plots of the curves and the data to see which fits seem most reasonable. Then try a more accurate fit by breaking the fit (and the integral) into two parts, say 0 to 25 K and 25 to 273 (or 298) K. The Mathematica notebook "MATH_366.STUD.nb" contains the data already typed in.

Problem 3 Calculate the equilibrium constant for the dissociation of bromine:

$$Br_2(g) = 2\,Br(g)$$

at 500 K and 1000 K assuming a temperature dependent $C_P(T)$ given by:

$$C_P\left[Br_2(g)\right] = a + bT + \frac{c}{T^2}$$

where $a = 37.32$ J K^{-1} mol^{-1}

$b = 0.50 \times 10^{-3}$ J K^{-2} mol^{-1}

$c = -1.26$ J K mol^{-1} .

For Br(g) use the ideal gas value of C_P. This approximation breaks down above 1000 K.

$$\Delta_{rxn}H^o_{298} = 192861 \text{ J}$$
$$\Delta_{rxn}G^o_{298} = 161682 \text{ J}$$

Compare your values with the literature values $K_p(500K) = 2.21 \times 10^{-15}$ and $K_p(1000K) = 3.27 \times 10^{-5}$. You'll need to use $\Delta G = \Delta H - T\Delta S$, $\Delta G = -RT\ln K_p$, integrate C_p to get ΔH, and integrate C_p/T to get ΔS. Once again, the Mathematica notebook "MATH_366.STUD.nb" contains the conveniently entered data.

References

A copy of the book *The Beginners Guide to Mathematica Version 2*, by Theodore W. Gray and Jerry Glynn (Addison-Wesley, Reading, MA, 1992) is available on campus. Note, however, that we use Mathematica Version 4, so some of the details may have changed. As you might have guessed, the authors have published *The Beginners Guide to Mathematica Version 4*, and it is available at the web site of Wolfram Research, the producers of Mathematica:

http://www.wolfram.com/

At the site, you can also view a copy of the most important Mathematica book, titled appropriately enough *The Mathematica Book*, by Stephen Wolfram, the person who developed Mathematica. A hard copy of this book comes when you purchase a copy of Mathematica for about $1,000. You have access to a software version of *Mathematica Book* when you are running Mathematica. You may also find this book in Schow QA76.95 .W65 1999: Stephen Wolfram, *The Mathematica Book*, 4th ed. (Wolfram Media, Champaign, IL, 1999). There are also numerous specialty books on Mathematica available, including *Mathematica Computer Programs for Physical Chemistry*, by William H. Cropper (Springer-Verlag, New York, 1998) with CD-ROM included.

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