THE ENTROPY OF LEAD

STUDENT INSTRUCTIONS

by

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These instructions accompany the Mathcad file cppbrun.mcd.

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Heat capacity measurements are a very important source of thermodynamic data. The substance is first cooled down to a very low temperature. Then definite amounts of energy ΔH are added to the system usually by a precisely calibrated electrical circuit. The temperature is usually measured by magnetic susceptibility determinations of a paramagnetic salt. $Cp = \Delta H/\Delta T$ at constant pressure.

Heat capacity measurements for metallic lead are stored on your disk in a file called cplead.prn. In the computational document the values are read into the computer.

The enthalpy change ΔH for the lead going from low temperature to high can be obtained by integration of the Cp vs T plot. The entropy change for a substance is dq_r / T for a reversible heat change at an absolute temperature T. So the entropy change ΔS for lead going from low temperature to high can be obtained by integration of the Cp/T vs T curve.

The data from these experiments consists of lists of temperatures and Cp values. We don't know an analytical function for which we can find the antiderivative and evaluate it at the upper and lower limits. In this case we must find the integral or the area under the curve by numerical methods. Often this is done using the trapezoid rule. The area is broken up into a series of trapezoids. The area of each trapezoid is simply the average of the values of the function multiplied by the distance between the points on the x axis.

$$A := \frac{f\left(x_{i+1}\right) + f\left(x_i\right)}{\left(x_{i+1} - x_i\right)\cdot 2}$$

If we should have evenly spaced points along the x axis then

$$Area := \frac{\left(f(x_1) + f(x_2)\right)\cdot\Delta x}{2} + \frac{\left(f(x_2) + f(x_3)\right)\cdot\Delta x}{2} ...$$

which simplifies to

$$Area := \frac{\left(f(x_1) + f(x_n)\right)\cdot\Delta x}{2} + \sum_{i=2}^{n-1} f(x_i)\cdot\Delta x$$

The Cp data for Pb are not evenly spaced. But MATHCAD can help us with this problem using the spline interpolation technique. In this method the derivative of the function is computed for each experimental point, and these values are used in an interpolation technique to find the value of the function at any point x_i. Then the values are substituted into the area expression for evenly spaced points.

EXERCISE 1

Determine the area for N=10, N=100, and N=1000. Which one is most accurate and why? You may recall that the definition of the definite integral involves taking the limit as Δx approaches 0.

Next note in the computational document (page 3) the small contribution to the entropy at temperatures lower than the lowest one measured.

EXERCISE 2

Carry through the integration (by hand) of the low temperature region indicated on page 3 (0 to T_1) to obtain the value of ΔS. Compare the total entropy at 298^o K with the value given in your textbook.

EXERCISE 3

Make changes in the MATHCAD document to obtain the enthalpy change ΔH as the substance is heated from absolute zero to 298^{o}K. Helpful hint: To get a subscript (as in T_i type ' [i ' and then the up arrow key to select the whole quantity T_i.

An alternative method to obtain the entropy is to evaluate the integral

$$\Delta S := \int_{lnT_1}^{lnT_2} Cp \, d(lnT)$$

this equation is toggled off

The function is often smoother and can be accurately integrated with a smaller number of points.

EXERCISE 4

Make changes in the MATHCAD computational document to carry out the alternate integration over Cp d(lnT).