The Entropy of Lead

Computational Document

by
George Hardgrove
Chemistry Department
St. Olaf College
Northfield, MN 55057

hardgrov@lars.acc.stolaf.edu

The instuctions for using this document are in the file cppbins.mcd

Translated from Mathcad to Mathematica by: Laura Rachel Yindra, Journal of Chemical Education, University of Wisconsin-Madison, August 2003.

The heat capacity data are located in a file called cplead. Values of Cp and absolute temperature are read into the computer. The computer then calculates values of ds = Cp/T for each temperature.

```
In[1]:= A := Import["cplead.dat", "Table"]
```

note: if Mathematica cannot find this file, open and evaluate cplead.nb

```
In[2]:= ndata := Length[A]

In[3]:= i := Range[0, ndata - 1]

In[4]:= T := A[[All, 1]]

In[5]:= Cp := A[[All, 2]]

In[6]:= dS := Cp / T
```

This assigns the columns of the A matrix to temperature and heat capacity vectors.

Next view the contents of these vectors.

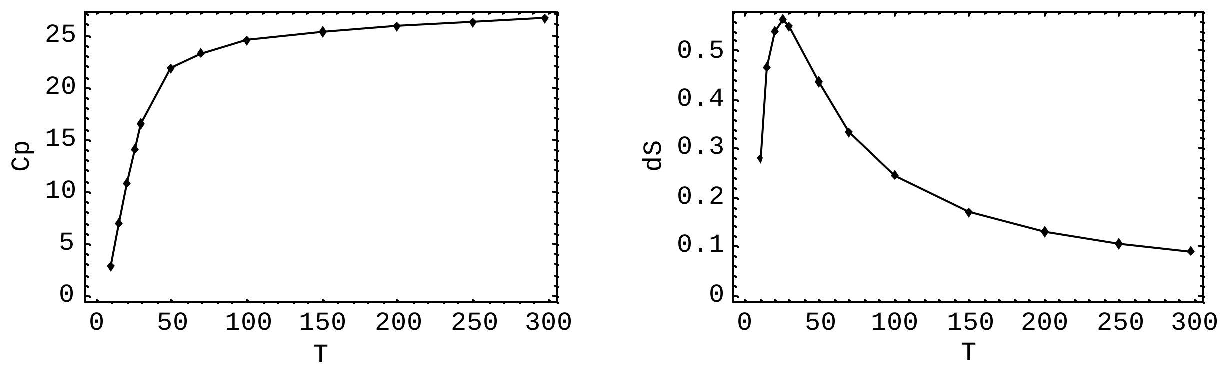
```
In[7]:= T

Out[7]= {10, 15, 20, 25, 30, 50, 70, 100, 150, 200, 250, 298}
```

```
In[8]:= Cp

Out[8]= {2.8, 7., 10.8, 14.1, 16.5, 21.8, 23.3, 24.5, 25.3, 25.8, 26.2, 26.6}

In[9]:= dS

Out[9]= {0.28, 0.466667, 0.54, 0.564, 0.55, 0.436,
         0.332857, 0.245, 0.168667, 0.129, 0.1048, 0.0892617}
```

Graph Setup

Graph

```
In[16]:=
        Show[GraphicsArray[{plot1, plot2}], DisplayFunction → $DisplayFunction]
```




```
Out[16]=
        - GraphicsArray -
```

To use the simple formula for trapezoid integration with evenly spaced points, we need to use interpolation methods. First we split up the space between the first and last points into n segments where we can adjust n.

```
In[17]:=
        n := 10

In[18]:=
        Δx = N[(Last[T] - T[[1]]) / (n)]

Out[18]=
        28.8

In[19]:=
        j := Range[0, n]
```

In[20]:=

```
x = T[[1]] + j Δx
```

Out[20]=

```
{10, 38.8, 67.6, 96.4, 125.2, 154., 182.8, 211.6, 240.4, 269.2, 298.}
```

We can now find the value of the function at each x[[j]]. On the graph below the black + signs are the experimental data, the red bars indicate the value of the function at evenly spaced points fx[j].

In[21]:=

```
fx := Interpolation[Table[{T[[i]], dS[[i]]}, {i, 1, ndata}]]
```

The evenly spaced points are put into the area formula

In[22]:=

```
area = Sum[Δx fx[x[[j]]], {j, 2, n}] + (fx[x[[1]]] + fx[x[[n + 1]]]) / 2 Δx
```

Out[22]=

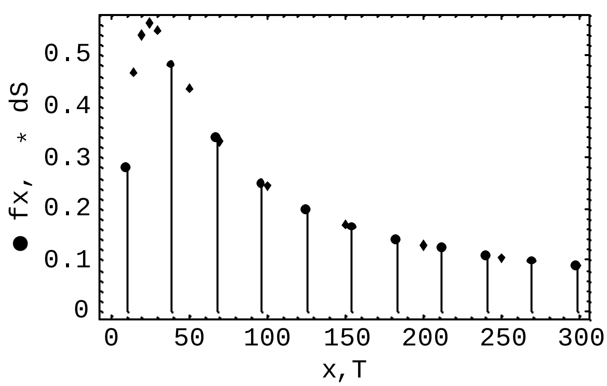
```
60.1231
```

Graph Setup

Graph

In[24]:=

```
Show[plot1, plot2, DisplayFunction → $DisplayFunction]
```



Out[24]=

```
- Graphics -
```

Now we need to consider the contribution to the entropy for the region from 0° K up to the lowest temperature at which the heat capacity was measured T[[0]]. In this region the heat capacity follows the function

$$Cp := a\,T^3$$

$$\frac{Cp}{T} := a\,T^2$$

$$\int_0^{T[[1]]} \frac{Cp}{T}\, dT := \frac{1}{3}\, Cp\, T[[1]]$$

In[25]:=

```
Cp[[1]]
```

Out[25]=

```
2.8
```

In[26]:=

$$\Delta S = \frac{Cp[[1]]}{3}$$

Out[26]=

```
0.933333
```

Therefore the total entropy for 0o K to 298° K is Area + S

In[27]:=

```
area + ΔS
```

Out[27]=

```
61.0565
```

The value reported in the literature is 64.81 J/Kmol. Increase the value of n above incrementally and see how the entropy determined by the area under the curve changes. The difference between the calculated and literature values is due to the method used to get the area under the curve.

In[28]:=

```
ClearAll[A, T, Cp, dS, ta, tb, plot1, plot2, n, Δx, x, fx, area, ΔS]
```