

### Solution 5.1

a) The simplest way to answer these questions is to calculate the forms for the equations in the different temperature regimes, evaluate the equations and store the data in a spreadsheet, and then generate the plots. Notice that the transformation temperatures are given in C not K in the first table. The molar heat capacity of the stable phase is given by integrating the heat capacity of the stable phase up to a transformation temperature where it jumps by the heat of transformation. This is expressed mathematically below.

$$\bar{H}(T) = \begin{cases} \bar{H}(298) + \int_{298}^T \bar{C}_p^\alpha dT & 298 \leq T < 395 \\ \bar{H}^\alpha(395) + \Delta\bar{H}_{\alpha \rightarrow \beta} + \int_{395}^T \bar{C}_p^\beta dT & 395 \leq T < 478 \\ \bar{H}^\beta(478) + \Delta\bar{H}_{\beta \rightarrow \gamma} + \int_{478}^T \bar{C}_p^\gamma dT & 478 \leq T < 591 \\ \bar{H}^\gamma(591) + \Delta\bar{H}_{\gamma \rightarrow \delta} + \int_{591}^T \bar{C}_p^\delta dT & 591 \leq T < 724 \\ \bar{H}^\delta(724) + \Delta\bar{H}_{\delta \rightarrow \epsilon} + \int_{724}^T \bar{C}_p^\epsilon dT & 724 \leq T < 749 \\ \bar{H}^\epsilon(749) + \Delta\bar{H}_{\epsilon \rightarrow l} + \int_{749}^T \bar{C}_p^l dT & 749 \leq T \leq 1000 \end{cases} \quad (1)$$

Upon substitution by the appropriate heat capacities and the heat of transformation (noting the different units given in the problem set), the analytic expression for the molar heat capacity of the stable phase is given below.

$$\bar{H}(T) = \begin{cases} 0 + 5.91(T - 298) + 2.9 \cdot 10^{-3}(T^2 - 298^2) & 298 \leq T < 395 \\ 768 + 800 + 5.21(T - 395) + 3.525 \cdot 10^{-3}(T^2 - 395^2) & 395 \leq T < 478 \\ 2256 + 150 + 2.98(T - 478) + 5.55 \cdot 10^{-3}(T^2 - 478^2) & 478 \leq T < 591 \\ 3413 + 130 + 9.0(T - 591) & 591 \leq T < 724 \\ 4740 + 20 + 8.4(T - 724) & 724 \leq T < 749 \\ 4970 + 440 + 8(T - 749) & 749 \leq T \leq 1000 \end{cases} \quad (2)$$

b) The molar entropy of the stable phase follows the same scheme as the molar enthalpy. We are not given the molar entropy of transformation but must calculate it from the following relation:  $\Delta\bar{S}_{trans} = \Delta\bar{H}_{trans}/T_{trans}$ .

$$\bar{S}(T) = \begin{cases} \bar{S}(298) + \int_{298}^T \bar{C}_p^\alpha / T dT & 298 \leq T < 395 \\ \bar{S}^\alpha(395) + \Delta\bar{S}_{\alpha \rightarrow \beta} + \int_{395}^T \bar{C}_p^\beta / T dT & 395 \leq T < 478 \\ \bar{S}^\beta(478) + \Delta\bar{S}_{\beta \rightarrow \gamma} + \int_{478}^T \bar{C}_p^\gamma / T dT & 478 \leq T < 591 \\ \bar{S}^\gamma(591) + \Delta\bar{S}_{\gamma \rightarrow \delta} + \int_{591}^T \bar{C}_p^\delta / T dT & 591 \leq T < 724 \\ \bar{S}^\delta(724) + \Delta\bar{S}_{\delta \rightarrow \epsilon} + \int_{724}^T \bar{C}_p^\epsilon / T dT & 724 \leq T < 749 \\ \bar{S}^\epsilon(749) + \Delta\bar{S}_{\epsilon \rightarrow l} + \int_{749}^T \bar{C}_p^l / T dT & 749 \leq T \leq 1000 \end{cases} \quad (3)$$

$$\bar{S}(T) = \begin{cases} 13.2 + 5.91 \log \frac{T}{298} + 2.9 \cdot 10^{-3}(T - 298) & 298 \leq T < 395 \\ 15.1 + 2.03 + 5.21 \log \frac{T}{395} + 3.525 \cdot 10^{-3}(T - 395) & 395 \leq T < 478 \\ 18.5 + 0.314 + 2.98 \log \frac{T}{478} + 5.55 \cdot 10^{-3}(T - 478) & 478 \leq T < 591 \\ 20.0 + 0.220 + 9.0 \log \frac{T}{591} & 591 \leq T < 724 \\ 22.1 + 0.0276 + 8.4 \log \frac{T}{724} & 724 \leq T < 749 \\ 22.4 + 0.587 + 8 \log \frac{T}{749} & 749 \leq T \leq 1000 \end{cases} \quad (4)$$

c) The molar Gibbs free energy of the stable phase is given by  $\overline{G} = \overline{H} - T\overline{S}$ . The calculation is done in the spreadsheet using full figures for enthalpy and entropy. The numbers are reduced to the correct number of significant figures after the calculation. Notice that for phase transformations at the equilibrium temperature and pressure  $\Delta\overline{G}_{trans} = 0$ .

$$\overline{G}(T) = \begin{cases} 298\overline{S}(298) + \int_{298}^T \overline{C}_p^\alpha dT - T \int_{298}^T \overline{C}_p^\alpha / T dT & 298 \leq T < 395 \\ \overline{G}^\alpha(395) + \int_{395}^T \overline{C}_p^\beta dT - T \int_{395}^T \overline{C}_p^\beta / T dT & 395 \leq T < 478 \\ \overline{G}^\beta(478) + \int_{478}^T \overline{C}_p^\gamma dT - T \int_{478}^T \overline{C}_p^\gamma / T dT & 478 \leq T < 591 \\ \overline{G}^\gamma(591) + \int_{591}^T \overline{C}_p^\delta dT - T \int_{591}^T \overline{C}_p^\delta / T dT & 591 \leq T < 724 \\ \overline{G}^\delta(724) + \int_{724}^T \overline{C}_p^\epsilon dT - T \int_{724}^T \overline{C}_p^\epsilon / T dT & 724 \leq T < 749 \\ \overline{G}^\epsilon(749) + \int_{749}^T \overline{C}_p^l dT - T \int_{749}^T \overline{C}_p^l / T dT & 749 \leq T \leq 1000 \end{cases} \quad (5)$$

Notice that the slope of this plot is negative as  $\frac{\partial \overline{G}}{\partial T} = -\overline{S}$  and  $\overline{S} \geq 0$  always. The curvature is negative as  $\frac{\partial^2 \overline{G}}{\partial T^2} = -\frac{\overline{C}_p}{T}$  and  $\overline{C}_p \geq 0$  and  $T \geq 0$  always.

d) The plot comes from the data evaluated in a spreadsheet. Notice that at phase transformations  $\overline{G}$  is constant while  $\overline{H}$  increases. This shows that if you add heat to plutonium at a temperature corresponding to an equilibrium transformation temperature the Gibbs free energy will remain constant until the heat added equals the heat of transformation. Also notice that in general,  $\overline{G}$  is a decreasing function of  $\overline{H}$ .

e) Assume the system is closed and the hot and cold parts do no work on each other.

$$0 = \Delta H_c + \Delta H_h \quad (6)$$

$$0 = 2\Delta \overline{H}_c + \Delta \overline{H}_h \quad (7)$$

$$2(\overline{H}(T_f) - \overline{H}(298)) = \overline{H}(1000) - \overline{H}(T_f) \quad (8)$$

$$\overline{H}(T_f) = \frac{\overline{H}(1000) - 2 * \overline{H}(298)}{3} = 2472.7 J/mole \quad (9)$$

Using the spreadsheet as a lookup tool. This corresponds to the final temperature of  $T_f = 486 K$ .

**bonus**

$\alpha$	primitive monoclinic
$\beta$	C-centered monoclinic
$\gamma$	face-centered orthorhombic
$\delta$	face-centered cubic
$\delta'$	body-centered tetragonal
$\epsilon$	body-centered cubic

## Solution 5.2

There are two possible solutions depending on how you interpret the definition of the COE. There is the engineering definition,  $\alpha = \frac{1}{L_0} \frac{\partial L}{\partial T}$  or the true definition,  $\alpha = \frac{1}{L} \frac{\partial L}{\partial T}$ . (Think about the difference between true and engineering strain.)

**Engineering answer** By rearranging the engineering definition for the coefficient of thermal expansion and integrating, we can arrive at an expression for the final temperature of the rod. Here,  $T_f$  is the final temperature,  $L_f$  is

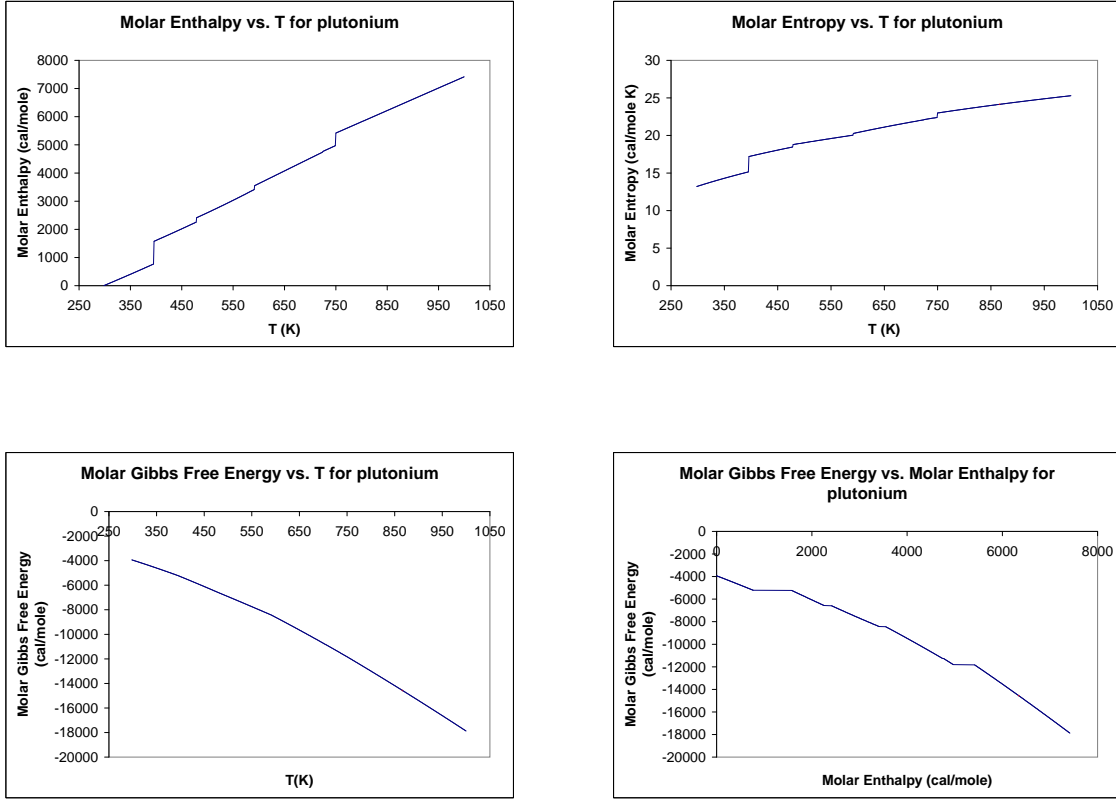


Figure 1: Plots of thermodynamic quantities for the stable phases of plutonium for question 5.1.

the final length of the rod.

$$T_f - T_i = \frac{L_f - L_i}{L_i} \frac{1}{\alpha} \quad (10)$$

Define the rate of change of bar length with change of the thermostat temperature setting as  $\beta = 0.005m/C$ . From this definition where  $T_0 = 20C$ , we rearrange to arrive at the following.

$$L_f - L_i = \beta(T_f - T_0) \quad (11)$$

Combining these expressions, we can solve for the final temperature.

$$T_f = \frac{1}{L_i \alpha - \beta} [L_i \alpha T_i - \beta T_0] \quad (12)$$

b) When  $L_i = \beta/\alpha$  then  $T_f$  is unbounded.

**“True” answer** By rearranging the “true” definition for the coefficient of thermal expansion and integrating, we can arrive at an expression for the final temperature of the rod.

$$T_f - T_i = \frac{1}{\alpha} \log \frac{L_f}{L_i} \quad (13)$$

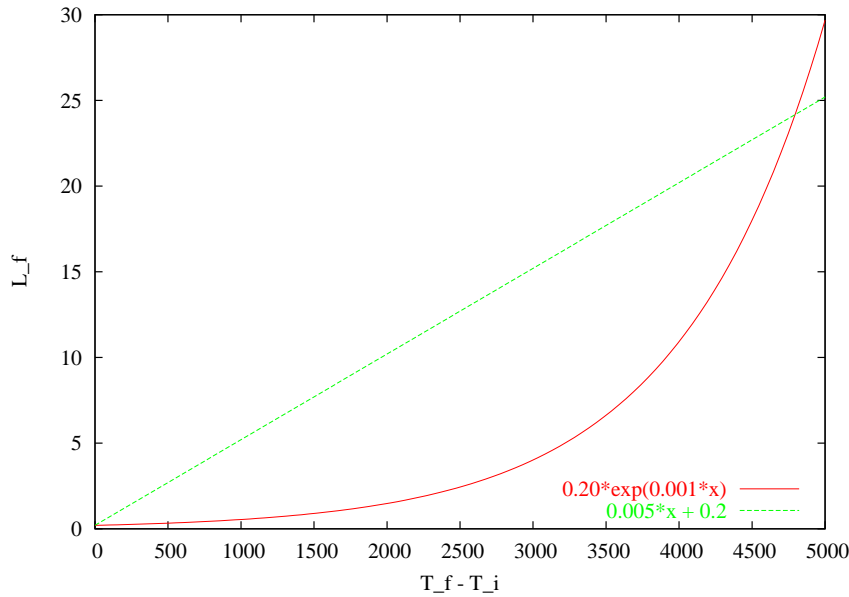
We can make use of the other relation,

$$L_f - L_i = \beta(T_f - T_i)$$

Use above relations to eliminate  $L_f$ ,

$$\beta(T_f - T_i) + L_i = L_i * \exp(\alpha(T_f - T_i)) \quad (14)$$

This equation falls into the category of transcendental equations that are generally hard to solve (for  $T_f$ ). A nice way to get information about the solutions of these kinds of equations is by graphical representation. The idea is to plot the LHS and the RHS of the above equation separately and examine where they intersect. A representative plot for  $\beta = 0.005$ ,  $L_i = 20\text{cm}$  and  $\alpha = 0.001$  is given below.



A trivial solution is  $T_f = T_i$  which is true for all values of  $\alpha$  (this means the thermostat remains pointing at the IC temperature forever.) However, as shown in the plot, there exists another temperature at which the length of the bar would be same as the height of the pointer corresponding to the IC temperature.

The condition for divergence or crazy thermostat is that the curves do not intersect at any other point apart from  $T_i = T_f$ . This can be deduced by comparing the slope of the linear term and slope of the exponential term at  $T_f = T_0$ .

slope of the line corresponding to the linear term (LHS) =  $\beta$ .

slope of the exponential term (RHS) (at  $T = T_f$ ) =  $\alpha L_i$ .

The condition for existence of a 'working' thermostat (where the diabolical attempt almost failed) is given by

$$\beta > \alpha L_i. \quad (15)$$

### Solution 5.3

In each part of this problem, it is necessary to calculate the intermediate equilibrium temperatures before calculating the entropy change of the isolated system of blocks.

**two by two**

ii.

$$\Delta H = 1/4 \int_{T_c}^{T_{ii}} \overline{C}_p dT + 1/4 \int_{T_h}^{T_{ii}} \overline{C}_p dT = 0 \quad (16)$$

$$1/4 \overline{C}_p (T_{ii} - T_c) + 1/4 \overline{C}_p (T_{ii} - T_h) = 0 \quad (17)$$

$$T_{ii} = \frac{T_c + T_h}{2} \quad (18)$$

iii.

$$\Delta H = 1/4 \int_{T_c}^{T_{iii}} \overline{C}_p dT + 1/2 \int_{T_{ii}}^{T_{iii}} \overline{C}_p dT + 1/4 \int_{T_h}^{T_{iii}} \overline{C}_p dT = 0 \quad (19)$$

$$1/4 \overline{C}_p (T_{iii} - T_c) + 1/2 \overline{C}_p (T_{iii} - T_{ii}) + 1/4 \overline{C}_p (T_{iii} - T_h) = 0 \quad (20)$$

$$T_{iii} = \frac{T_c + T_h}{2} \quad (21)$$

In each of these symmetric processes, the equilibrium temperature is  $\frac{T_c + T_h}{2}$ . The total entropy change is given by the sum of the entropy change from processes i and ii.

$$\begin{aligned} \Delta S &= 1/4 \int_{T_c}^{T_{ii}} \overline{C}_p / T dT + 1/4 \int_{T_h}^{T_{ii}} \overline{C}_p / T dT + \\ &1/4 \int_{T_c}^{T_{iii}} \overline{C}_p / T dT + 1/2 \int_{T_{ii}}^{T_{iii}} \overline{C}_p / T dT + 1/4 \int_{T_h}^{T_{iii}} \overline{C}_p / T dT \\ \Delta S &= 1/4 \overline{C}_p \left( \log \frac{T_{ii}}{T_c} + \log \frac{T_{ii}}{T_h} + \log \frac{T_{iii}}{T_c} + 2 \log \frac{T_{iii}}{T_{ii}} + \log \frac{T_{iii}}{T_h} \right) \\ \Delta S &= \frac{1}{2} \log \frac{T_c + T_h}{4 T_c T_h} \end{aligned}$$

**four by four**

Once again, in this problem due to the symmetric nature of each equilibration the final temperature for each intermediate step is  $T_{ii} = T_{iii} = T_{vi} = T_v = \frac{T_c + T_h}{2} = T_f$ .

Therefore, the total entropy change is given by the following.

$$\begin{aligned}
\Delta S &= 1/8 \int_{T_c}^{T_f} \overline{C_p}/T dT + 1/8 \int_{T_h}^{T_f} \overline{C_p}/T dT + \\
&1/8 \int_{T_c}^{T_f} \overline{C_p}/T dT + 1/4 \int_{T_f}^{T_f} \overline{C_p}/T dT + 1/8 \int_{T_h}^{T_f} \overline{C_p}/T dT + \\
&1/8 \int_{T_c}^{T_f} \overline{C_p}/T dT + 1/2 \int_{T_f}^{T_f} \overline{C_p}/T dT + 1/8 \int_{T_h}^{T_f} \overline{C_p}/T dT + \\
&1/8 \int_{T_c}^{T_f} \overline{C_p}/T dT + 3/4 \int_{T_f}^{T_f} \overline{C_p}/T dT + 1/8 \int_{T_h}^{T_f} \overline{C_p}/T dT \\
\Delta S &= 4 * 1/8 \overline{C_p} \left( \log \frac{T_f}{T_c} + \log \frac{T_f}{T_h} \right) \\
\Delta S &= \frac{1}{2} \log \frac{T_c + T_h}{4T_c T_h}
\end{aligned}$$

$2^n$  by  $2^n$

From the previous two cases it is obvious that the entropy change of the isolated system of blocks for any case with the symmetry of the previous cases is the same  $\Delta S = \frac{1}{2} \log \frac{T_c + T_h}{4T_c T_h}$ . This is because the general expression is  $\Delta S = \frac{n}{2n} \log \frac{T_c + T_h}{4T_c T_h}$  and the n's cancel out.