Exercise 5.1

Pure plutonium forms six different equilibrium solids at atmospheric pressure. The room temperature equilibrium phase, $\delta$, is monoclinic.

<table>
<thead>
<tr>
<th>Transition (phase 1 $\rightarrow$ phase 2)</th>
<th>$\Delta \overline{H}$ (K Cal mole$^{-1}$)</th>
<th>$T_{eq}^\text{trans}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha \rightarrow \beta$</td>
<td>0.8</td>
<td>122</td>
</tr>
<tr>
<td>$\beta \rightarrow \gamma$</td>
<td>0.15</td>
<td>205</td>
</tr>
<tr>
<td>$\gamma \rightarrow \delta$</td>
<td>0.13</td>
<td>318</td>
</tr>
<tr>
<td>$\delta \rightarrow \epsilon$</td>
<td>0.02</td>
<td>451</td>
</tr>
<tr>
<td>$\epsilon \rightarrow$ liquid</td>
<td>0.44</td>
<td>476</td>
</tr>
</tbody>
</table>

The standard enthalpy of formation (i.e., the zero of the enthalpy scale of Pu at STP) is $\overline{H}(T = 298K, P = 1atm) = 0$ and the entropy at STP is $\overline{S}(T = 298K, P = 1atm) = 13.2$cal/°mole. The molar heat capacities are given by

<table>
<thead>
<tr>
<th>phase of Pu</th>
<th>$C_p$ (cal/°mole)</th>
<th>temperature range (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$5.91 + 5.8 \times 10^{-3}T$</td>
<td>298-395</td>
</tr>
<tr>
<td>$\beta$</td>
<td>$5.21 + 7.05 \times 10^{-3}T$</td>
<td>395-480</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$2.98 + 11.1 \times 10^{-3}T$</td>
<td>480-588</td>
</tr>
<tr>
<td>$\delta$</td>
<td>9.0</td>
<td>588-753</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>8.4</td>
<td>753-913</td>
</tr>
<tr>
<td>liquid</td>
<td>8</td>
<td>913-$T_{\text{boil}}$</td>
</tr>
</tbody>
</table>

(a) Calculate the molar enthalpy of the most stable phase of Pu and plot it as a function of temperature from $T = 298K$ to $T = 1000K$.

(b) Calculate the molar entropy of the most stable phase of Pu and plot it as a function of temperature from $T = 298K$ to $T = 1000K$.

(c) Calculate the molar Gibbs free energy of all phases of Pu and plot it as a function of temperature from $T = 298K$ to $T = 1000K$.

(d) Plot the molar Gibbs free energy of all phases as a function of the molar enthalpy for temperatures from $T = 298K$ to $T = 1000K$.

(e) Suppose $\alpha$-Pu at 273K is mixed with liquid Pu at 1000K in the ration of 2:1. What would be the resulting equilibrium phase?
5% Extra Credit: Find the crystal structures of each of the stable phases.

**Exercise 5.2**

The coefficient of linear thermal expansion is defined as:

\[ \alpha_T = \frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_{\sigma=0} \]

That is, the rate that a bar of length \( L \) decreases its length with temperature if no load \( (\sigma = 0) \) is applied to the bar—per unit length of the bar.

In a diabolical attempt to defeat the thermostat that controls the temperature along the infinite corridor, you decide to weld a stiff bar of length \( L_{\text{initial}} \) at an initial temperature of \( T_{\text{initial}} \) to the thermostat switch that controls the temperature along the I.C.

![Diagram](image)

**Figure 5-2-i:** The set-up I.C. for the I.C. hack.

(a) Assuming that \( \alpha \) is a constant, the I.C. has an initial temperature of 20°C, and the degree marks on the thermostat are separated by 5mm each, find an expression for the equilibrium temperature of the I.C. as a function of \( L_{\text{initial}} \) and \( T_{\text{initial}} \).

(b) Are there sets of lengths \( L_{\text{initial}}(T_{\text{initial}}) \) for which the temperatures are unbounded?
10% Extra Credit: Plot the isotherms of equilibrium temperature in the $L_{\text{initial}}-T_{\text{initial}}$ plane.

**Exercise 5.3**

In this problem, the entropy change of the universe is be calculated for different ways of bringing two blocks at different temperatures and composed of the same material to equilibrium.

Assume the initial configuration is 1/2 mole of material at temperature $T_C$ and 1/2 mole of material at temperature $T_H$. The molar heat capacity, $C_P$, is constant between $T_C$ and $T_H$ and there are no phase transitions between $T_C$ and $T_H$.

Calculate the entropy change of the universe (which is composed only of the two blocks which do no work on each other) for the following methods of equilibration:

**two by two**

i. Each 1/2 mole block is divided in two equal parts of 1/4 mole (assume no entropy change to produce the 4 1/4 mole blocks).

ii. One 1/4 mole block at $T_C$ is placed in contact with one 1/4 mole block at $T_H$ and a new equilibrium system of 1/2 mole is obtained (some entropy).

iii. The one remaining 1/4 mole block at $T_C$ and the one remaining 1/4 mole block at $T_H$ are both placed in contact with the equilibrium composite system that was equilibrated in the previous step (some more entropy).

**four by four**

i. Each 1/2 mole block is divided in four equal parts of 1/8 mole.

ii. One of the 1/8 mole blocks at $T_C$ is brought into equilibrium with one of the 1/8 mole blocks at $T_H$.

iii. One of the 1/8 mole blocks at $T_C$ and one of the 1/8 mole blocks at $T_H$ are brought into equilibrium with the 1/4 mole block produced in the previous step.

iv. One of the 1/8 mole blocks at $T_C$ and one of the 1/8 mole blocks at $T_H$ are brought into equilibrium with the 1/2 mole block produced in the previous step.

iv. One of the 1/8 mole blocks at $T_C$ and one of the 1/8 mole blocks at $T_H$ are brought into equilibrium with the 3/4 mole block produced in the previous step.

**2^n by 2^n**

i. Each 1/2 mole block is divided in $2^n$ equal parts of $1/2^{n+1}$ mole.

ii. One of the $1/2^{n+1}$ mole blocks at $T_C$ is brought into equilibrium with one of the $1/2^{n+1}$ mole blocks at $T_H$.

iii. One of the $1/2^{n+1}$ mole blocks at $T_C$ and one of the $1/2^{n+1}$ mole blocks at $T_H$ are brought into equilibrium with the block produced in the previous step.

: 

n. One of the $1/2^{n+1}$ mole blocks at $T_C$ and one of the $1/2^{n+1}$ mole blocks at $T_H$ are brought into equilibrium with the block produced in the previous step.