

## Solutions to Problem Set 5

### Exercise 2.1

Consider heating a body  $A$ , of constant heat capacity  $1\text{J}/^\circ\text{C}$  and initially at temperature  $100\text{K}$ , to a final temperature of  $200\text{K}$ . The heating takes place by sequentially placing it in thermal contact with  $N$  different large thermal reservoirs (so large that their temperature does not change during thermal contact).

For example,

$N=1$  The body  $A$  is placed in contact with a single reservoir at  $200\text{K}$ .

$N=2$  The body  $A$  first attains thermal equilibrium with a one reservoir at  $T=150\text{K}$ ; subsequently, it attains thermal equilibrium with the second at  $T=200\text{K}$ .

$N = M$  The body  $A$  first attains thermal equilibrium with a one reservoir at  $T = (100 + 100/M)\text{K}$ . Next, it attains equilibrium with a reservoir at  $T = (100 + 2 \times 100/M)\text{K}$ . . . . Next, it attains equilibrium with a reservoir at  $T = (100 + j \times 100/M)\text{K}$ . . . . Finally,  $A$  attains equilibrium with a reservoir at  $T = (100 + M \times 100/M)\text{K}$ .

On the same graph, plot the change in (1) entropy of the body  $A$  and (2) the change in entropy of the universe as a function of  $1/N$ .

### Solution:

In general, at constant pressure with constant  $C_P$  where  $A$  stands for the body  $A$ ,  $u$  for the universe and  $r$  for the reservoir,  $T_0$  is the initial temperature and  $T_f$  is the final temperature, the change in entropy of the body  $A$  is given by:

$$\Delta S_A = \int_{T_0}^{T_f} \frac{C_P}{T} dT = C_P \ln\left(\frac{T_f}{T_0}\right)$$

and the change in entropy of the universe is given by:

$$\Delta S_u = \Delta S_A + \Delta S_r = \Delta S_A + \frac{\Delta H_r}{T_r}$$

Using *First Law*:

$$\Delta H_r = -\Delta H_A = \int_{T_0}^{T_f} C_P dT = C_P(T_f - T_0)$$

So, the final expression for the change in entropy of the universe is:

$$\Delta S_u = \Delta S_A - C_P \frac{T_f - T_0}{T_f}$$

We calculate first the change in entropy of the body  $A$  varying the number of reservoirs between the  $100\text{K}$  and  $200\text{K}$  interval:

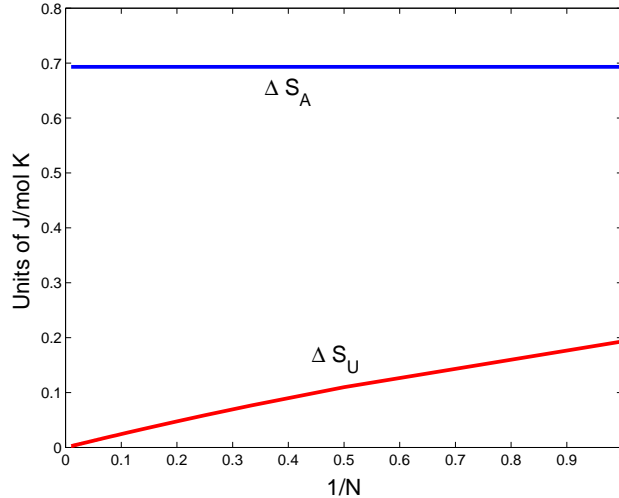
- For  $N = 1$ ,  $\Delta S_A = C_P \ln\left(\frac{200\text{ K}}{100\text{ K}}\right) = C_P \ln(2)$
- For  $N = 2$ ,  $\Delta S_A = C_P \left(\ln\left(\frac{150\text{ K}}{100\text{ K}}\right) + \ln\left(\frac{200\text{ K}}{150\text{ K}}\right)\right) = C_P \ln\left(\frac{150 \cdot 200}{100 \cdot 150}\right) = C_P \ln(2)$
- For  $N = 4$ ,  $\Delta S_A = C_P \left(\ln\left(\frac{125\text{ K}}{100\text{ K}}\right) + \ln\left(\frac{150\text{ K}}{125\text{ K}}\right) + \ln\left(\frac{175\text{ K}}{150\text{ K}}\right) + \ln\left(\frac{200\text{ K}}{175\text{ K}}\right)\right) = C_P \ln\left(\frac{125 \cdot 150 \cdot 175 \cdot 200}{100 \cdot 125 \cdot 150 \cdot 175}\right) = C_P \ln(2)$
- For  $N = M$ ,  $\Delta S_A = C_P \ln(2)$

This means that the change in entropy of system A is path independent, i.e. it is a state function whose value is given by the initial and final conditions.

For the change in entropy of the universe we have:

- For  $N = 1$ :  $\Delta S_u = \Delta S_A - C_P \frac{200-100}{200}$
- For  $N = 2$ :  $\Delta S_u = \Delta S_A - C_P \left[\frac{150-100}{150} + \frac{200-150}{200}\right]$
- For  $N = 4$ :  $\Delta S_u = \Delta S_A - C_P \left[\frac{125-100}{125} + \frac{150-125}{150} + \frac{175-150}{175} + \frac{200-175}{200}\right]$
- For  $N = M$ :  $\Delta S_u = \Delta S_A - C_P \sum_j^N \frac{100(1+\frac{j}{N})-100(1+\frac{j-1}{N})}{100(1+\frac{j}{N})} = \Delta S_A - C_P \sum_j^N \frac{1}{j+N}$

In the limit when N is large, the sum in the above expression converges to the value of  $C_P \ln(2)$ . Therefore, in the limit of a quasistatic process, the entropy change in the universe is zero. The change in the Gibbs free energy of the system is also zero (local condition for equilibrium). This indicates that a quasistatic process follows a path of equilibrium processes:



## Exercise 2.2

Consider the phase transformation of pure carbon graphite to pure carbon diamond at atmospheric pressure and at temperatures between 298 and 1200K.

Using the data:

graphite	Standard molar enthalpy	$\overline{H}(T = 298, P = 1\text{atm}) = 0$
graphite	Molar entropy	$\overline{S}(T = 298, P = 1\text{atm}) = 5.694 \frac{\text{J}}{\text{mole}^\circ\text{K}}$
graphite	Molar heat capacity	$\overline{C}_P(T = 298, P = 1\text{atm}) = 17.2 + 4.27T - \frac{8.79 \times 10^{-5}}{T^2} \frac{\text{J}}{\text{mole}^\circ\text{K}}$
diamond	Standard molar enthalpy	$\overline{H}(T = 298, P = 1\text{atm}) = 1900 \frac{\text{J}}{\text{mole}}$
diamond	Molar entropy	$\overline{S}(T = 298, P = 1\text{atm}) = 2.44 \frac{\text{J}}{\text{mole}^\circ\text{K}}$
diamond	Molar heat capacity	$\overline{C}_P(T = 298, P = 1\text{atm}) = 9.12 + 13.2T - \frac{6.19 \times 10^{-5}}{T^2} \frac{\text{J}}{\text{mole}^\circ\text{K}}$

1. Draw an accurate plot of the molar change in molar enthalpy for graphite transforming to diamond at 1 atm pressure for temperatures between 298 and 1200K.
2. Draw an accurate plot of the molar change in Gibb's free energy for graphite transforming to diamond at 1 atm pressure for temperatures between 298 and 1200K.
3. Draw an accurate plot of each of the molar free energies for diamond and for graphite as a function of the entropy of the system at 1 atm pressure for temperatures between 298 and 1200K.

**Solution:**

1. We first must find an expression for the enthalpies of diamond and graphite. Using  $C_P \equiv \frac{\partial H}{\partial T}$ , we have:  $H = \int_{T_i}^{T_f} C_P dT + H(T_i)$

$$\overline{H}_{\text{graphite}} = 17.2T_f + 2.135T_f^2 + \frac{.879e - 4}{T_f} - 194722.14$$

$$\overline{H}_{\text{diamond}} = 9.12T_f + 6.6T_f^2 + \frac{.619e - 4}{T_f} - 586924.1601$$

$$\overline{\Delta H} = -8.08T_f + 4.465T_f^2 - \frac{.26e - 4}{T_f} - 392202.0201$$

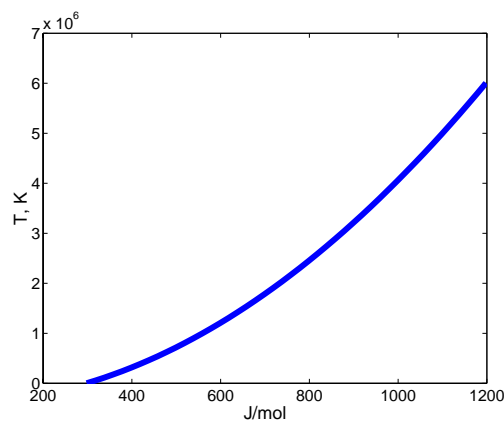


Figure 1:  $\overline{\Delta H}$  vs.  $T$

2. To calculate  $\Delta G$  we need first to calculate  $\Delta S$ . By using  $\bar{S} = \int_{T_i}^{T_f} \frac{C_P}{T} dT + S_{T_i}$ :

$$\begin{aligned}\bar{S}_{graphite} &= 4.27T_f + \frac{.4395e - 4}{T_f^2} + 17.2 \ln(T_f) - 1364.756008 \\ \bar{S}_{diamond} &= 13.2T_f + \frac{.3095e - 4}{T_f^2} + 9.12 \ln(T_f) - 3983.117493 \\ \overline{\Delta S} &= 8.93T_f - \frac{.13e - 4}{T_f^2} - 8.08 \ln(T_f) - 2618.361485\end{aligned}$$

The Gibbs free energies can be calculated using  $G = H - TS$ :

$$\begin{aligned}\bar{G}_{graphite} &= 1381.956008T_f - 2.135T_f^2 + \frac{.4395e - 4}{T_f} - 194722.1400 - 17.2T_f \ln(T_f) \\ \bar{G}_{diamond} &= 3992.237493T_f - 6.6T_f^2 + \frac{.3095e - 4}{T_f} - 586924.1601 - 9.12T_f \ln(T_f) \\ \overline{\Delta G} &= 2610.281485T_f - 4.465T_f^2 - \frac{.13e - 4}{T_f} - 392202.0201 + 8.08T_f \ln(T_f)\end{aligned}$$

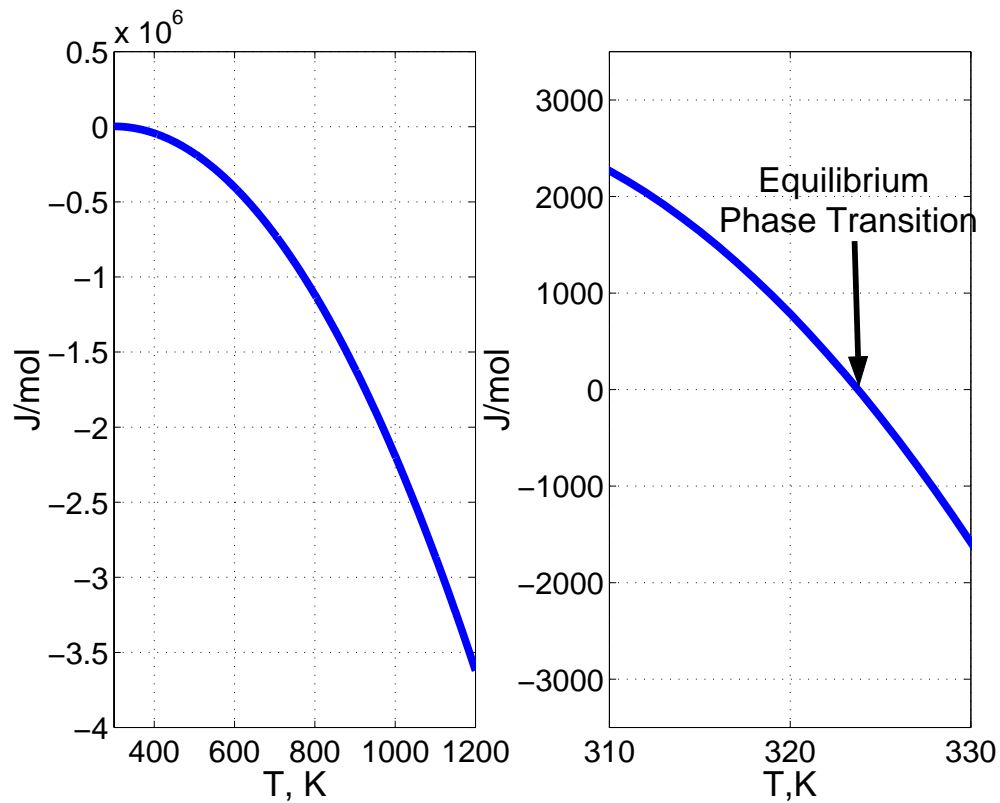


Figure 2:  $\overline{\Delta G}$  vs.  $T$

It is evident from fig 2 that there occurs a phase transition. This transition is located at the point where  $\Delta G = 0$ . From the algebraic expression for  $\Delta G$  we find that  $T_{Transition} \simeq 323.755K$ .

3. The parametric plots of  $\overline{G}(T)$  vs.  $\overline{S}(T)$ :

### Exercise 2.3

A quantity of super-cooled liquid Mn at 800K is adiabatically solidified into its equilibrium solid phase at constant pressure. From the data below, calculate what fraction of the Mn will have solidified and the final temperature of the system.

Transition (phase 1 $\rightarrow$ phase 2)	$\Delta \overline{H}$ ( $\frac{J}{mole}$ )	$T_{eq}^{trans}$ (K)
$\alpha \rightarrow \beta$	2010	993
$\beta \rightarrow \gamma$	2300	1373
$\gamma \rightarrow \delta$	1800	1409
$\delta \rightarrow$ liquid	13400	1517

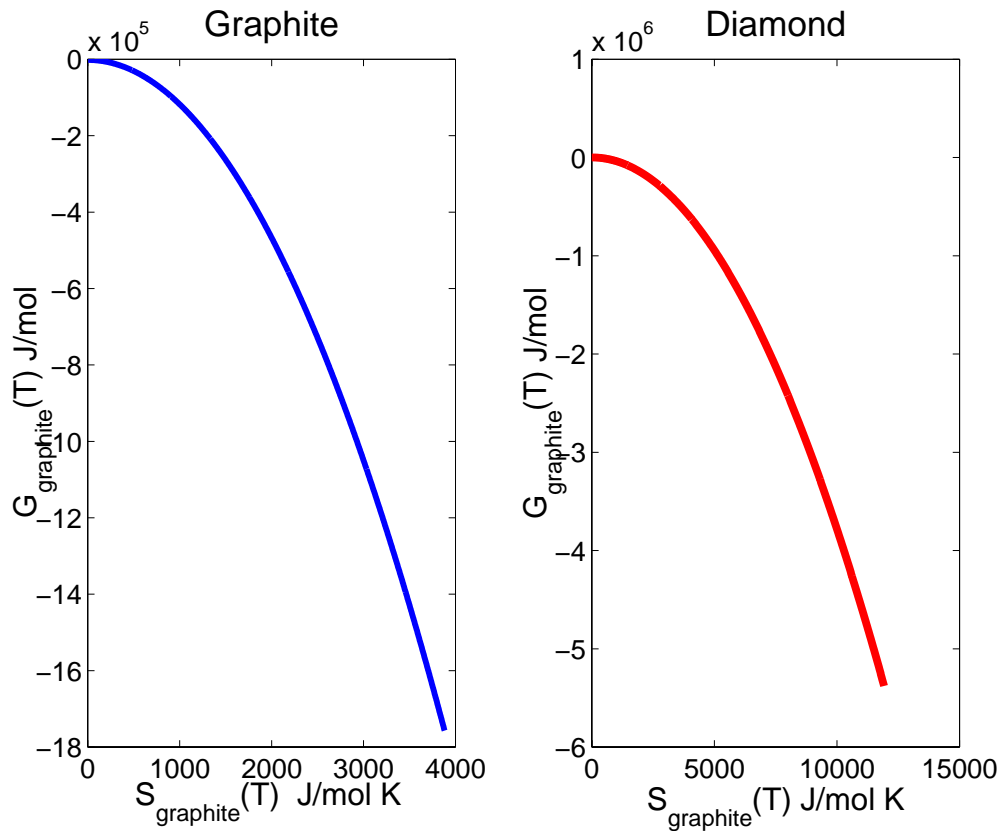


Figure 3:  $\overline{G(T)}$  vs.  $\overline{S(T)}$  for both graphite and diamond

phase of Mn	$\overline{C_p}$ ( $\frac{\text{J}}{\text{mole}^\circ\text{K}}$ )	temperature range (K)
$\alpha$	$21.6 + 15.9T$	298-993
$\beta$	$34.9 + 2.8T$	993-1373
$\gamma$	44.8	1373-1409
$\delta$	47.3	1409-1517
liquid	46.0	1517- $T_{boil}$

**Solution:**

The first thing to do is use  $H = \int_{T_i}^{T_f} C_P dT + H(T_i)$  to calculate the enthalpies for all the phases. Note that  $H(T_i)$  for all phases other than  $\alpha$  would be  $H_{previous\ phase}(T_{Transition}) + \Delta H_{Transition}$ :

$$\begin{aligned}
 H_\alpha &= -712428.6 + 21.6 T + 7.95 T^2 \quad \text{for } T = 298 \dots 993 \text{ K} \\
 H_\beta &= 5734995.450 + 34.9 T + 1.4 T^2 \quad \text{for } T = 993 \dots 1373 \text{ K} \\
 H_\gamma &= 8362883.350 + 44.8 T \quad \text{for } T = 1373 \dots 1409 \text{ K} \\
 H_\delta &= 8361160.850 + 47.3 T \quad \text{for } T = 1409 \dots 1517 \text{ K} \\
 H_{liquid} &= 8374462.950 + 46.0 T \quad \text{for } T = 1517 \dots T \text{ K}
 \end{aligned}$$

We are told that liquid is cooled to 800 K without allowing it to solidify, This means that

we are not allowing for any nucleation to happen.

By using a linear fit, an expression for the enthalpy of the liquid as a function of temperature can be obtained:

$$\overline{H}_{liq} = 8.37446295e6 + 4.6 T$$

It is possible to extrapolate this expression to 800 K, since this enthalpy is calculated using material properties.

We are told that the liquid solidifies adiabatically at 800 K, therefore, by using *First Law*:

$$dH = dQ + V dP = 0$$

This means that once the liquid has reached 800 K, the enthalpy of the system **remains constant**. Many people used this expression to establish that since  $\Delta H = 0$ , there would be no phase transformation whatsoever, which is wrong, since we are allowing the liquid to solidify to the equilibrium  $\alpha$  phase:

What  $\Delta H = 0$  means is that there will be no heat released to the environment, and therefore all the heat released by the solidification ( $-\Delta H_{melt}$ ) would remain in the system. Therefore, once the liquid solidifies into  $\alpha$ , it needs to raise its temperature and further transform into other phases (if necessary) in order to keep the initial enthalpy unchanged. This might be better understood by examining the next figure:

From fig 4 it can be seen that the liquid transforms entirely into the  $\beta$  phase, and the final temperature reached by the system is  $T \sim 1370 K$ .

The final temperature can be precisely calculated by equating the enthalpy of the metastable liquid at 800 K to the enthalpy of the  $\beta$  phase:

$$H_{liquid,800K} = 8.41126295e6 = 5734995.450 + 34.9 T + 1.4 T^2$$

By solving this quadratic equation, the final temperature of the system is calculated to be  $T = 1370.2 K$

Note: The *clever way* to solve this problem was by graphically realizing where the final state of the system was supposed to be and then estimate what the final temperature of the system was.

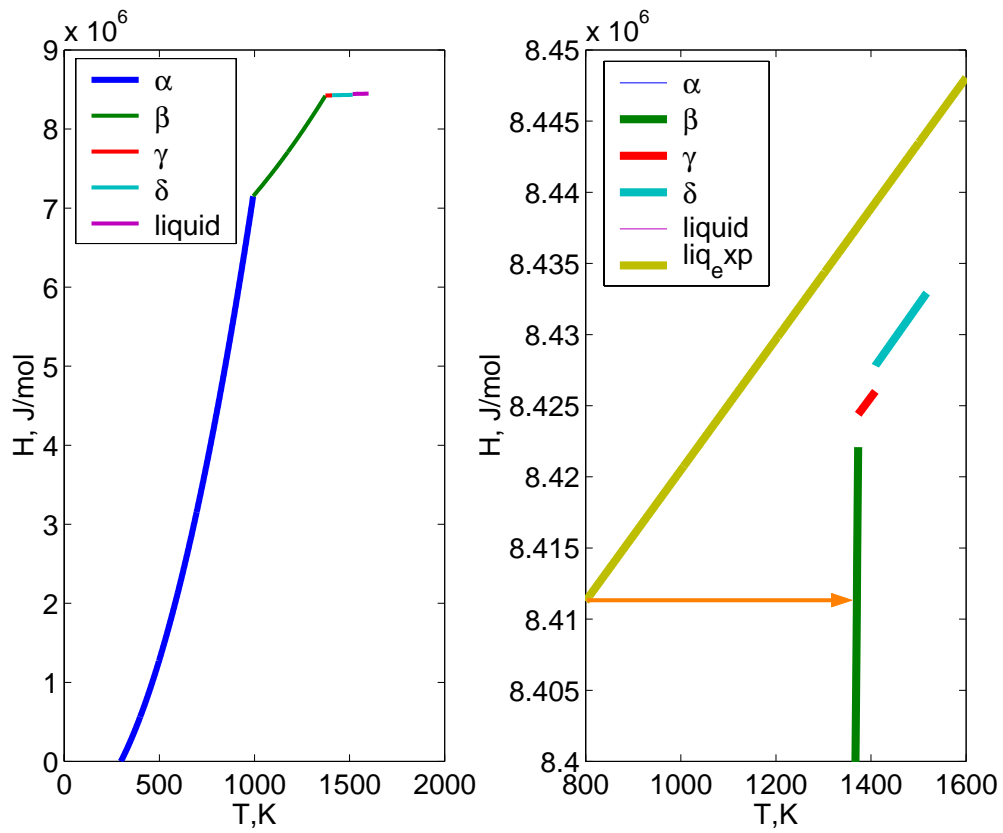


Figure 4: Change in enthalpy of the system as a function of Temperature. The arrow points to the final state of the system.