

### Graded Problems: THERMODYNAMICS

3. **Transforming materials.** Elemental manganese has several phase transitions among different solid states in the temperature range 800 – 1500 K. The constant pressure heat capacity of Mn can be modeled by the polynomial expression:

$$C_p = a + bT + \frac{c}{T^{-2}} \left( \frac{J}{mole\ K} \right)$$

Constants for the heat capacity of manganese, along with relevant temperature and enthalpies of transformation are:

Phase	Stable Temperature Range (K)	a	b	c	$\Delta H_{trans}$ (J/mole)
$\alpha$	298 – 993	21.6	.0159	0	-
$\alpha \rightarrow \beta$	-	-	-	-	2010
$\beta$	993 – 1373	34.9	.0028	0	-
$\beta \rightarrow \gamma$	-	-	-	-	2300
$\gamma$	1373 – 1409	44.8	0	0	-
$\gamma \rightarrow \delta$	-	-	-	-	1800
$\delta$	1409 – 1517	47.3	0	0	-
$\delta \rightarrow liquid$	-	-	-	-	12958
<i>liquid</i>	$T_m < T < T_{boil}$	46	0	0	-

- a. Using this data, calculate the entropy change for heating 1 mole of Mn from 860 K to 1400 K at constant pressure.

The total entropy change is arrived at by (1) integrating the constant pressure heat capacity in segments and (2) accounting for the jumps in entropy at the phase transitions:

$$C_p = \left( \frac{dq}{dT} \right)_p = T \left( \frac{dS}{dT} \right)_p$$

$$dS = \frac{C_p(T)}{T} dT$$

$$\Delta S_{860-993} = \int_{860}^{993} \frac{C_p(T)}{T} dT = \int_{860}^{993} \frac{21.6 + 0.0159T}{T} dT = 5.22 \frac{J}{K}$$

at the  $\alpha \rightarrow \beta$  phase transition. The entropy of formation corresponding to this transformation is:

$$\Delta S_{\alpha \rightarrow \beta} = \frac{\Delta H_{\alpha \rightarrow \beta}}{T_{\alpha \rightarrow \beta}} = \frac{2010}{993} = 2.02 \frac{J}{K}$$

We proceed similarly with the integrations for the rest of the temperature increase:

$$\begin{aligned}\Delta S_{993-1373} &= 12.37 \frac{J}{K} \\ \Delta S_{\beta \rightarrow \gamma} &= \frac{2300}{1373} = 1.68 \frac{J}{K} \\ \Delta S_{1373-1400} &= 0.872 \frac{J}{K}\end{aligned}$$

Thus,

$$\begin{aligned}\Delta S_{TOTAL} &= \Delta S_{860-993} + \Delta S_{\alpha \rightarrow \beta} + \Delta S_{993-1373} + \\ &\quad \Delta S_{\beta \rightarrow \gamma} + \Delta S_{1373-1400} = 22.16 \frac{J}{K}\end{aligned}$$

- b. Suppose 1 mole of Mn is supercooled (cooled below its stable solidification temperature without transformation to the solid) to a temperature of 1000 K then *adiabatically* allowed to solidify into its stable form at constant pressure. Determine what final phase is formed, the fraction that has solidified, and the final temperature of the system.

The solution is most easily described graphically, after plotting the behavior of enthalpy as a function of temperature over the temperature range of interest.

Shown below is the calculated total enthalpy change between the solid  $\alpha$  phase at 800 K and the liquid phase at 1600 K, along with the paths of supercooling and subsequent adiabatic solidification that were specified in the problem. The restriction of *constant enthalpy* on the adiabatic process dictates the horizontal white arrow path moving to the equilibrium  $\beta$  phase.

*Because heat cannot transfer out of the system, the system is forced along an isenthalpic line.. This is not a process that transforms the solid isothermally—temperature changes because the heat that is expelled during the transformation from liquid to solid cannot leave the system. Thus, as solidification proceeds, the heat expelled is used up in immediately raising the temperature of the system isenthalpically until the system reaches the point on the equilibrium curve that intersects the isenthalpic line.*

To determine the temperature value quantitatively, we can calculate the enthalpy of the supercooled liquid relative to some arbitrary reference point in the liquid phase and find the temperature on the equilibrium curve that matches the resultant change in enthalpy.

For example, if we determine the enthalpy of the supercooled liquid at 1000 K relative to the liquid at the melting point, we have:

$$H_{T_M}^L - H_{1000\text{ K}}^L = \int_{1000\text{ K}}^{T_M} C_p^L dT$$

We write down this difference and keep it somewhere safe, because we'll need it again in a few lines.

Remember, enthalpy is a state function, and state functions make life easy. We can simply start at *the same* arbitrary point in the liquid state that we chose above (I believe we chose  $T_M$ ), and follow the equilibrium enthalpy-temperature curve instead of the supercooling curve. We follow the equilibrium curve until we find that temperature  $T_{final}$  that gives us the same value for  $\Delta H$  that we stored for safekeeping.

Without the graph, one might start by guessing that we are in the  $\beta$  phase:

$$H_{T_M}^L - H_{1000\text{ K}}^L \stackrel{??}{=} H_{T_M}^L - H_{1373\text{ K}}^\beta$$

$$H_{T_M}^L - H_{1373\text{ K}}^\beta = \Delta H_M + \int_{1409\text{ K}}^{T_M} C_p^\delta dT + \Delta H_{\gamma \rightarrow \delta} + \int_{1373\text{ K}}^{1409\text{ K}} C_p^\delta dT + \Delta H_{\beta \rightarrow \gamma}$$

We find that we could be in the  $\beta$  phase because

$$H_{T_M}^L - H_{1000\text{ K}}^L > H_{T_M}^L - H_{1373\text{ K}}^\beta$$

so we search for a temperature  $T_{final}$  in the  $\beta$  phase that would give us  $\Delta H = H_{T_M}^L - H_{1000\text{ K}}^L$ :

$$H_{T_M}^L - H_{1000\text{ K}}^L = H_{T_M}^L - H_{1373\text{ K}}^\beta + \int_{T_{final}}^{1373} C_p^\beta dT$$

Indeed, we find that there is a solution (you can punch this into your calculator or use some sort of mathematical software to do all of this—I used Mathematica):

$$T_{final} \sim 1370\text{ K}$$

and the supercooled liquid lies entirely within the  $\beta$  phase.

4. **Why is it hard to make measurements at constant volume?** We have discussed in class that, experimentally,  $C_v$  is difficult to measure due to thermal expansion. Let's quantify this difficulty: Suppose you have 1 mole of iron that has a volume of  $7.31\text{ cm}^3$  at  $293\text{ K}$ . Determine the pressure that would have to be applied after this material is heated to  $298\text{ K}$  (only 5 degrees warmer!) to compress it to the volume it had at  $293\text{ K}$ —thus maintaining constant volume.

Data for Fe:

$$\alpha = 6.3 \times 10^{-5} \text{ K}^{-1}$$

$$\kappa = 1.10 \times 10^{-6} \text{ atm}^{-1} \quad \text{at } 298 \text{ K}$$

We can use the properties of state functions again since we are dealing with changes in  $V, T, p$ .

We start with the formula for the thermal expansion coefficient in order to calculate the amount of expansion that occurs when the temperature is raised to 298 K. At constant pressure:

$$\begin{aligned}\alpha &= \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p \\ \alpha dT &= \frac{dV}{V} \\ \int_{T_L}^{T_H} \alpha dT &= \int_{V_L}^{V_H} \frac{dV}{V} \\ \alpha(T_H - T_L) &= \alpha \Delta T = \ln \left( \frac{V_H}{V_L} \right)\end{aligned}$$

Thus the volume after heating is:

$$V_H = V_L e^{\alpha \Delta T}$$

We want to next determine the pressure we need to compress the material back to  $V_L$ :

$$\begin{aligned}\kappa &= -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T \\ dP &= -\frac{1}{\kappa V} dV \\ \Delta P &= -\frac{1}{\kappa} \int_{V_H}^{V_L} \frac{dV}{V} = \frac{1}{\kappa} \ln \frac{V_H}{V_L} = \frac{1}{\kappa} \ln \frac{V_L e^{\alpha \Delta T}}{V_L} = \frac{\alpha \Delta T}{\kappa} = 286.3 \text{ atm}\end{aligned}$$

This is the difficulty in making constant volume measurements.