COURSE 3.20: THERMODYNAMICS OF MATERIALS

FINAL EXAM, Dec 16, 2002

PROBLEM 1  (12 POINTS)___________
PROBLEM 2  (12 POINTS)___________
PROBLEM 3  (10 POINTS)___________
PROBLEM 4  (14 POINTS)___________
PROBLEM 5  (12 POINTS)___________
PROBLEM 6  (10 POINTS)___________
PROBLEM 7  (16 POINTS)___________
PROBLEM 7  (14 POINTS)___________

TOTAL     (100 POINTS) ____________

You can either write your answer on the question sheets or use separate pages. In each case make sure your answer is clearly marked.

A neat answer is the sign of a clear mind
Question 1:

Consider a closed system at constant volume composed of a very large number N of distinguishable subsystems which do not interact with each other upon forming the larger system. The subsystem can only be in one of two energy states: $E = 0$, or $E = \varepsilon$.

a) What is the maximum possible value of the energy per subsystem ($E_{\text{tot}}/N$) when the system is in equilibrium (at any thermodynamic condition)?

b) In this condition of maximum energy, what is the entropy of the total system ($S_{\text{tot}}/N$)?

c) Sketch the heat capacity, $C_V$, of the system as function of temperature. Pay particular attention to limiting values (e.g. what is the value of the heat capacity at $T = 0$ and how is that value approached; value at high temperature, etc.)
Question 2:

One mole of a diatomic ideal gas initially having a volume of 1 liter and temperature of 800 K is made to undergo a three step cycle:

1 -> 2 reversible isothermal expansion to a volume of 2 liters
2-->3 reversible adiabatic compression to the original volume of 1 liter
3-->1 reversible (heating or cooling) at constant volume to the original temperature of 800 K.

a) draw the reversible paths of this cycle on a P-V diagram
b) calculate the values of P and T at states 1, 2 and 3
c) calculate the change in entropy of the gas along each path
d) Assume now that the adiabatic compression from 2-->3 (i.e. from 2 liters to 1 liter) had occurred irreversibly. Would we end up with a higher or lower pressure $P_3$ than the one calculated in part (b) after the reversible adiabatic compression?

DATA: $C_p$ for the gas is $7/2 \, R$; $C_v$ is $5/2 \, R$; $\Delta H_{\text{evap}} = 20 \, \text{kJ/mole}$
Question 3:

The natural variables for the Helmholtz free energy, $F$, are $V$ and $T$, giving the differential of $dF$ a particularly simple form when written in terms of $dV$ and $dT$.

Write the differential $dF$ in terms of variations in $T$ and $p$. Do not leave any partial differentials in the expression for $dF$, but express everything in terms of properties or state functions ($C_p$, $C_v$, $U$, $H$, $S$, …)
Question 4:

Do not draw more than one solution. Clearly specify your answer

Below is the Mn-Mo phase diagram.

a) The phase boundaries in the area that is circled (near 2220°C) are somewhat unclear. Please draw a possible (but thermodynamically correct) solution for the three-phase equilibria near 2220°C showing clearly how all single phase regions connect to the invariant three-phase equilibrium. If necessary, exaggerate, the width of single phase regions. Please do not draw on the phase diagram, but make a clear drawing below. You do not need to draw the complete phase diagram, only the relevant section involving Mo, G and L near 2220°C. Do not yet worry about the hashed rectangle, which is for part b of the question.
b) Your advisor spilled beer over part of the phase diagram, and as a result the region that is hashed on the previous page became illegible. On the diagram, below, please sketch a plausible solution for the missing region.
Question 5:

$\text{Y}_2\text{O}_3$-$\text{ZrO}_2$ is a material of interest for sensors and solid oxide fuel cells. At the relevant temperature and composition range $\text{ZrO}_2$ forms a simple fluorite structure with an fcc array of Zr cations, and the oxygen ions occupying all the tetrahedral interstitials of this array.

As $\text{Y}_2\text{O}_3$ is added to $\text{ZrO}_2$, the Y cations substitute on the Zr sublattice. For charge compensation reasons, a vacancy needs to exist on the oxygen sublattice for each 2 Y cations added.

a) Assuming an ideal solution of Y and Zr on the cation sublattice, and oxygen and vacancies on the anion sublattice, write down the entropy of mixing as function of the mole fraction of Y cations on the cation sublattice.

b) In the real material, oxygen vacancies may be attracted to the Y cation, for electrostatic reasons or due to size effects. Describe how the entropy in part a) will change when such attractive interaction occurs.
Question 6:

Pure A melts at T=1000 K while pure B melts at T=1750 K. An fcc solid solution of A and B can be modeled with a regular solution model with enthalpy of mixing:

\[ \Delta H_{mix} = -12,600 \times X_A \times X_B \text{ in J/mol} \] (\( X_A \) is the mole fraction of A and \( X_B \) is the mole fraction of B).

Calculate the heat that evolves upon mixing 3 moles of pure liquid A with 7 moles of pure solid B at T=1200 K. It is observed that the final equilibrium state is a solid solution on the fcc lattice.

\[ \Delta H_{melt} = 4 \text{ kJ/mol} \] for pure A
\[ \Delta H_{melt} = 7 \text{ kJ/mol} \] for pure B
\[ \Delta C_P \text{ (Liquid – solid)} = 0 \text{ J/mol K} \] for pure A
\[ \Delta C_P \text{ (Liquid – solid)} = 2 \text{ J/mol K} \] for pure B
Question 7 (Short questions):

a) Define the Legendre transform of the entropy that gives a function with natural variables $1/T$ and $p/T$.

b) A material (closed system) at constant pressure undergoes a reversible phase transition with temperature at $T = T_0$. Please indicate whether the following statements are always true, true only part of the time, or never true.

*At the phase transition temperature the high temperature phase has a higher volume than the low-temperature phase:*

- NEVER TRUE
- ALWAYS TRUE
- TRUE PART OF THE TIME

*At the phase transition temperature $T_0$, the high temperature phase has a higher entropy than the low-temperature phase:*

- NEVER TRUE
- ALWAYS TRUE
- TRUE PART OF THE TIME

*At the phase transition temperature $T_0$, the high temperature phase has a higher enthalpy than the low-temperature phase:*

- NEVER TRUE
- ALWAYS TRUE
- TRUE PART OF THE TIME

*At the phase transition temperature $T_0$, the high temperature phase has a higher Gibbs free energy than the low-temperature phase:*

- NEVER TRUE
- ALWAYS TRUE
- TRUE PART OF THE TIME

(c) A metal always has a higher electronic entropy than an oxide

- TRUE
- FALSE
d) For a system with only pdV work, in an environment under constant pressure and temperature, the condition that $\Delta S_{\text{universe}} > 0$ is equivalent to:

$$\Delta G > 0 \quad \Delta G < 0 \quad \Delta H < 0 \quad \Delta H > 0 \quad \Delta S < 0$$

$$\Delta S > 0$$

*In the above, the state functions (G,H,S) refer to properties of the system.*

e) At constant composition, does the free energy increase or decrease with increasing temperature?

$$\text{INCREASE} \quad \text{DECREASE}$$
Question 8:

Two crystallographic phases $\alpha$ and $\beta$ coexist at temperature $T$. The $\alpha$ phase is insoluble to B atoms and is made up exclusively of A atoms. The $\beta$ phase consists of both A and B atoms.

Assume that the atoms in the $\alpha$ and $\beta$ phases can be modeled as atoms on a lattice that do not interact with their neighbors, but independently vibrate around the equilibrium positions with the following characteristic frequencies:

- $\nu^\alpha_A$ for A atoms in the alpha phase leading to a single-particle partition function $q^\alpha_A$
- $\nu^\beta_A$ for A atoms in the beta phase leading to a single-particle partition function $q^\beta_A$
- $\nu^\beta_B$ for B atoms in the beta phase leading to a single-particle partition function $q^\beta_B$.

a) Write an explicit expression for the single-particle partition function $q^\alpha_A$ in terms of the vibrational frequency $\nu^\alpha_A$.

b) Derive an expressions for the free energies of $\alpha$ and $\beta$ in terms of the single particle partition functions.

c) Write an expression for the solubility limit of A in $\beta$. 