

NAME: _____

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 $E = \epsilon$.

- a) What is the maximum possible value of the energy per subsystem (E_{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_{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 .

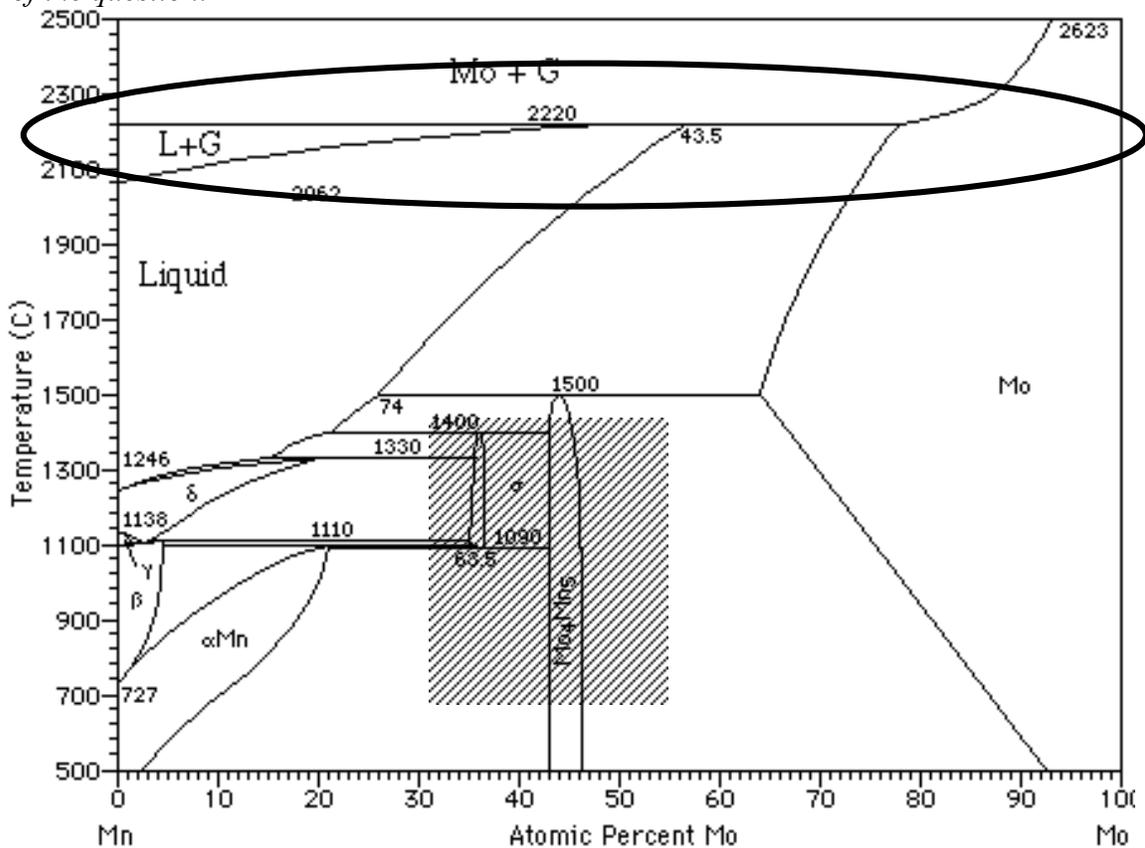
Write the differential dF in terms of variations in T and p . Do not leave any partial differentials in the expression for dF , but express everything in terms of properties or state functions (C_p , C_v , U , H , S , ...)

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.



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 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 Y_2O_3 is added to 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:

$\Delta H_{\text{mix}} = -12,600 X_A X_B$ 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.

$\Delta H_{\text{melt}} = 4$ kJ/mol for pure A

$\Delta H_{\text{melt}} = 7$ kJ/mol for pure B

ΔC_P (Liquid – solid) = 0 J/mol K for pure A

ΔC_P (Liquid – solid) = 2 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:

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

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?

_____ INCREASE _____ DECREASE

Question 8:

Two crystallographic phases α and β coexist at temperature T . The α phase is insoluble to B atoms and is made up exclusively of A atoms. The β phase consists of both A and B atoms.

Assume that the atoms in the α and β 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:

ν_A^α for A atoms in the alpha phase leading to a single-particle partition function q_A^α

ν_A^β for A atoms in the beta phase leading to a single-particle partition function q_A^β

ν_B^β for B atoms in the beta phase leading to a single-particle partition function q_B^β .

- a) Write an explicit expression for the single-particle partition function q_A^α in terms of the vibrational frequency ν_A^α .
- b) Derive an expressions for the free energies of α and β in terms of the single particle partition functions.
- c) Write an expression for the solubility limit of A in β .