Department of

MATERIALS SCIENCE AND ENGINEERING

Doctoral Written Exam

Day 2

Core Areas covered:

ADVANCED THERMODYNAMICS OF MATERIALS
KINETICS ND PHASE TRANSFORMATIONS
STRUCTURE OF MATERIALS

Friday, January 26, 2007

Department of Materials Science and Engineering

DOCTORAL WRITTEN EXAM – Day 2
January 26, 2007

Your exam packet for day 2 contains a total of nine (9) questions from three (3) core areas, ADVANCED THERMODYNAMICS OF MATERIALS, KINETICS ND PHASE TRANSFORMATIONS, STRUCTURE OF MATERIALS, plus 20 answer sheets. Each question is on a separate page. A copy of the Table of Constants is included for your reference. **You must submit 2 questions from each core area for grading**. You will have 6 hours to complete the questions. You can obtain extra answer sheets from the proctor, if needed. Please use the following procedure:

Write a four (4) digit code of your choice, and your name on the 3 X 5 card provided. Use this code in place of your name to identify all answer sheets you submit for both days of the exam. Renee will keep the code information, sealed in an envelope, until after the exams are graded.

For each answer, use the question sheet as the first page of your answer. If additional pages are required, use the blank answer sheets provided. At the end of the examination, staple each question sheet and corresponding answer sheets for each question separately, put this instruction sheet on top of the questions you are turning in, and place them in one side of your exam folder. Place all other exam pages in the other side of your folder, and return everything to the proctor, or Renee if you finish before 2:30 P.M.

Please be sure to complete the information required on each page.

GOOD LUCK!

CODE NUMBER ________________

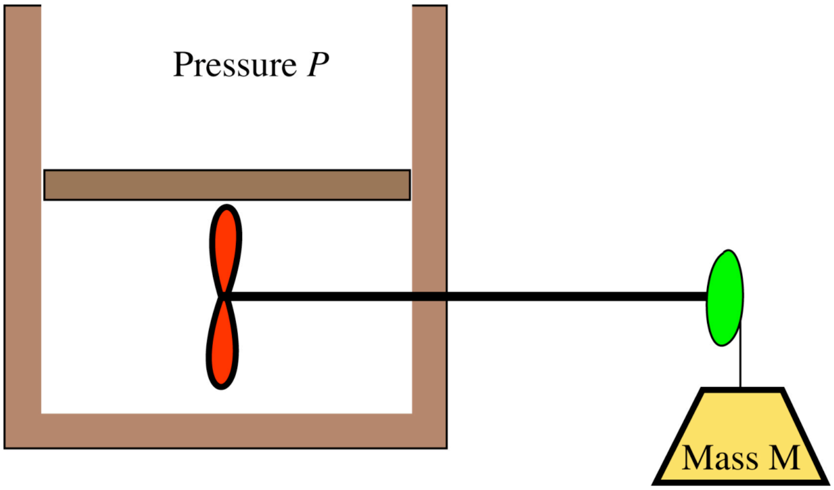
CHECK THE 6 QUESTIONS YOU WISH TO HAVE GRADED:

Advanced Thermodynamics Of Materials	Kinetics and Phase Transformations	Structure of Materials
1.______	4.______	7.______
2.______	5.______	8.______
3.______	6.______	9.______

Day 2 – ADVANCED THERMODYNAMICS OF MATERIALS CODE #________

1.

A fluid is held in a container that is covered with a frictionless piston. The container and piston are thermally insulated (no heat exchange with the environment) and the environment is at constant pressure *P*. A paddle is placed within the container, which is rotated by dropping a weight of mass *M* attached to a frictionless pulley contraption (see figure). Assume that the mass *M* drops by a distance *h*.



You are lucky in that the response functions for this fluid, C_p, C_V, β (thermal expansion coefficient at constant *P*) and κ (compressibility at constant *T*) happen to have been measured and are tabulated. It also turns out that they are constant within a large temperature interval.

a) Does the fluid undergo a reversible or irreversible change of state?
b) Derive an expression for the change in temperature ΔT between the final equilibrated state after *M* has been dropped and the initial state before *M* is dropped. Write your answer in terms of *M*, *h* and response functions of the fluid.
c) Derive a similar expression for the change in volume ΔV.

2.

A solid, crystalline oxide AO_{1-x} is susceptible to oxygen loss. Oxygen loss results in the creation of a dilute concentration of oxygen vacancies x over the oxygen sublattice. Assume that the crystal of an oxide AO_{1-x} has M cation sites (for the A atoms) and M oxygen sites. Denote n as the number of oxygen sublattice sites that are vacant such that $x=n/M$, and denote N as the number of oxygen atoms in the crystal, i.e. $n=M-N$.

The perfect oxide (without vacancies) has an energy E_p relative to a particular reference state of the individual A and O atoms. The energy cost to form an oxygen vacancy is ΔE_O (i.e. change in energy of the oxide as an oxygen atoms is removed from the crystal and put in its reference state). For any number of oxygen vacancies n, you can assume that the energy of the oxide is independent of how the oxygen vacancies are arranged over the oxygen sublattice.

a) For n oxygen vacancies, write down an expression for the total energy of the oxide.

b) The oxide is in equilibrium with air, which has a constant oxygen chemical potential μ_O. At constant T, V, N_A and μ_O derive an expression for the characteristic potential in terms of the internal energy and other relevant thermodynamic state variables.

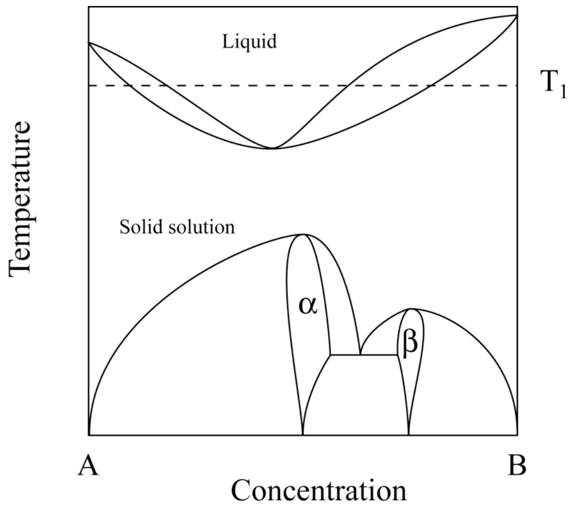
c) Write down an expression for the appropriate partition function Z for the thermodynamic boundary conditions of part (b) and determine a closed-form expression for Z by explicitly summing over all relevant microstates.

d) Derive an expression for the equilibrium oxygen vacancy concentration x as a function of temperature T and oxygen chemical potential μ_O.

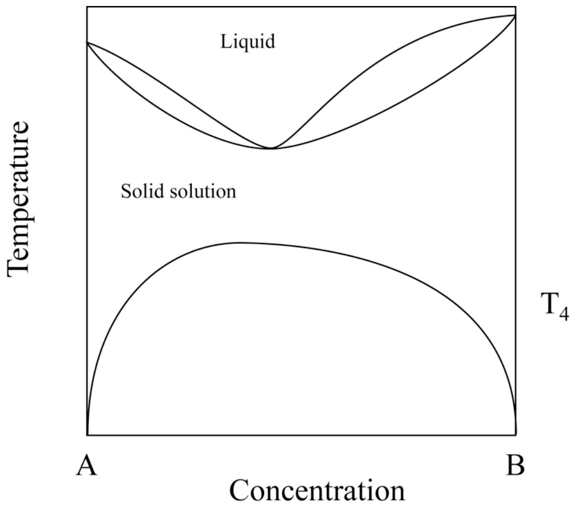
3.

(Five parts)

a) The phase diagrams of two alloys (alloy 1 and alloy 2) are illustrated below. In which of the two alloys is there an energetic tendency for the A and B atoms to attract each other? Briefly explain your answer.

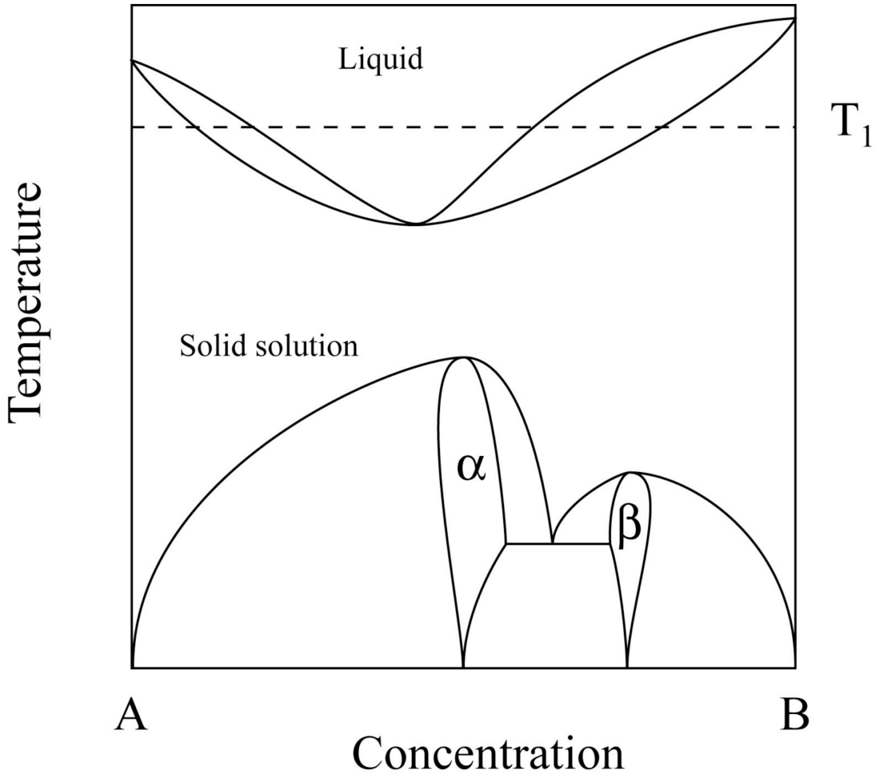


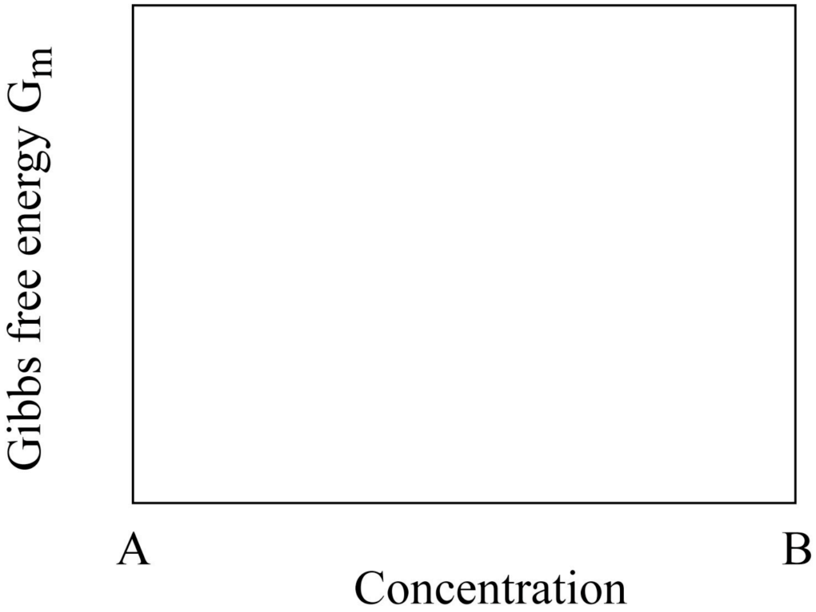
Alloy 1



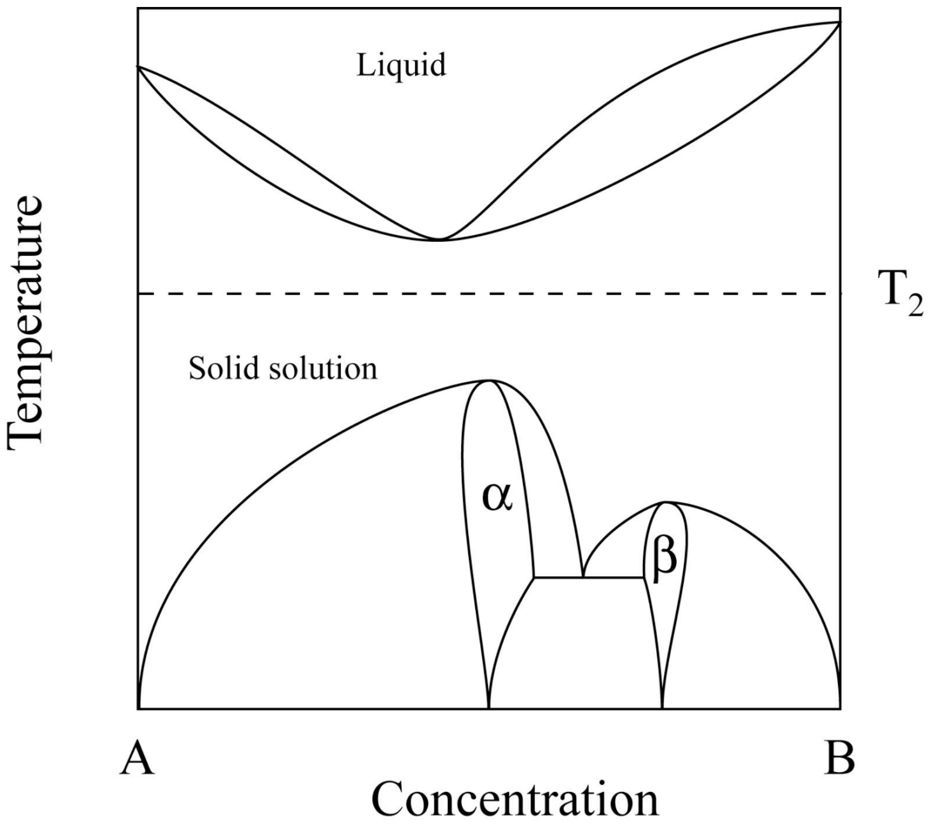
Alloy 2

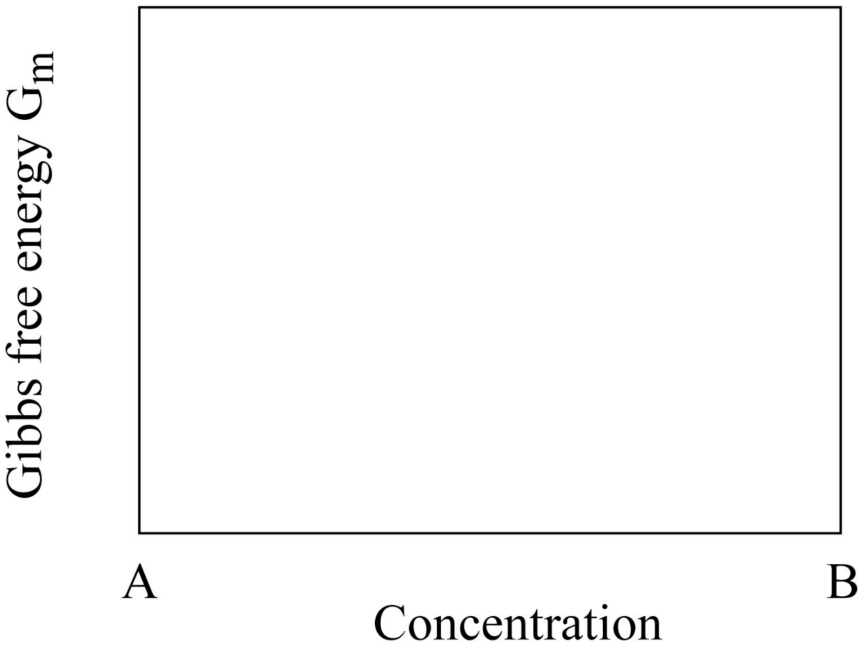
b) Schematically draw the free energy curves of the A-B alloy at temperature T_1. Make sure to label all your free energy curves.



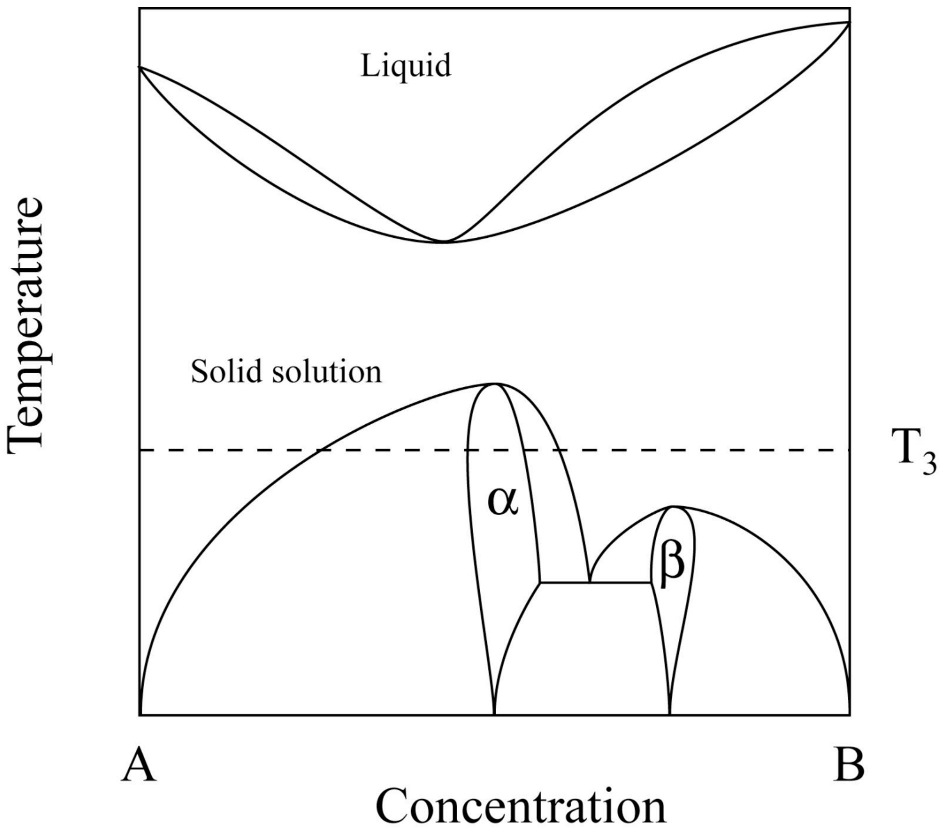


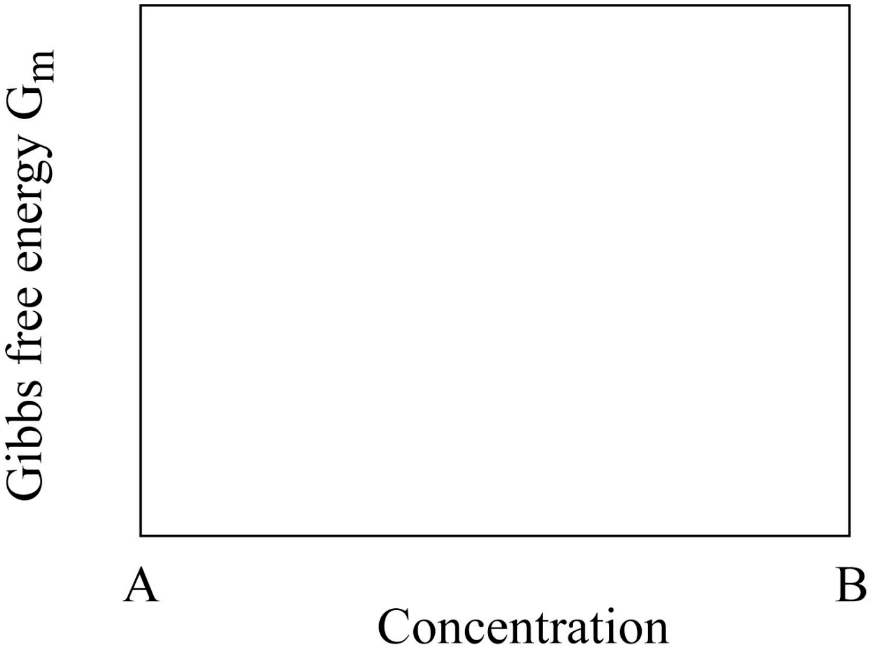
c) Schematically draw the free energy curves of the A-B alloy at temperature T_2. Make sure to label all your free energy curves.



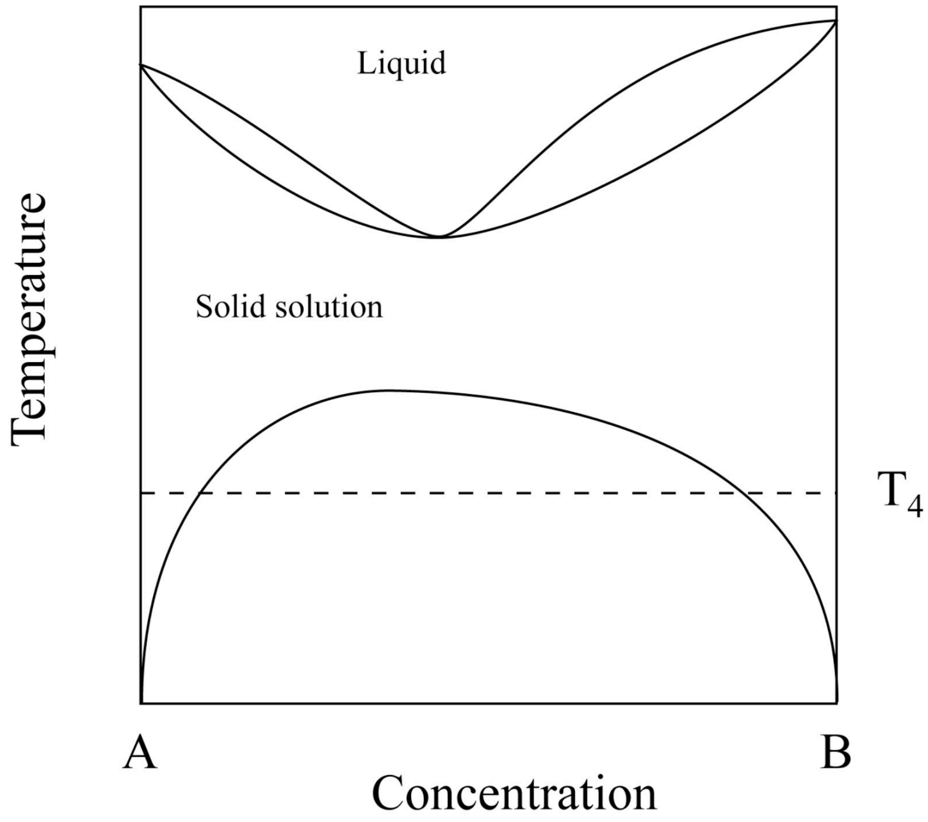


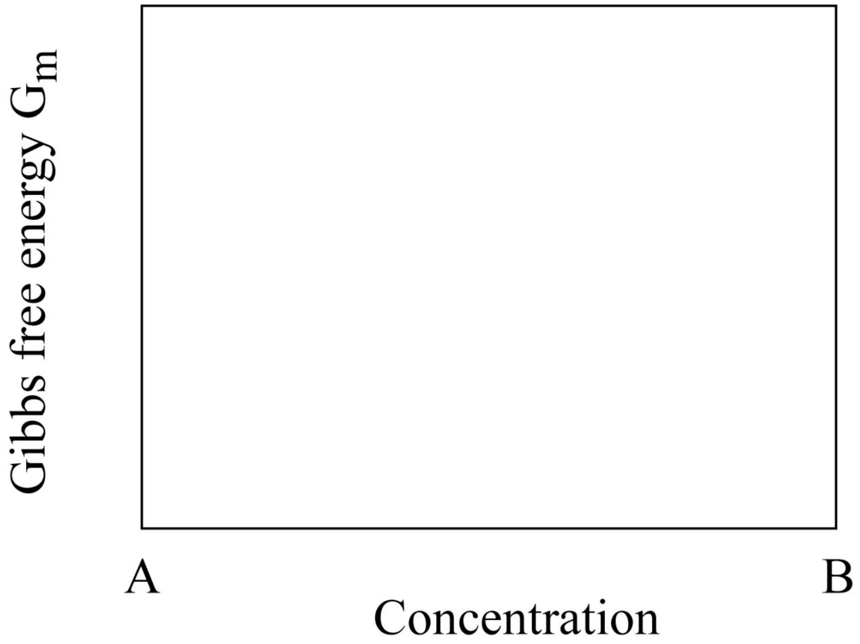
d) Schematically draw the free energy curves of the A-B alloy at temperature T_3. Make sure to label all your free energy curves.





e) Schematically draw the free energy curves of the A-B alloy at temperature T_4. Make sure to label all your free energy curves.





4.

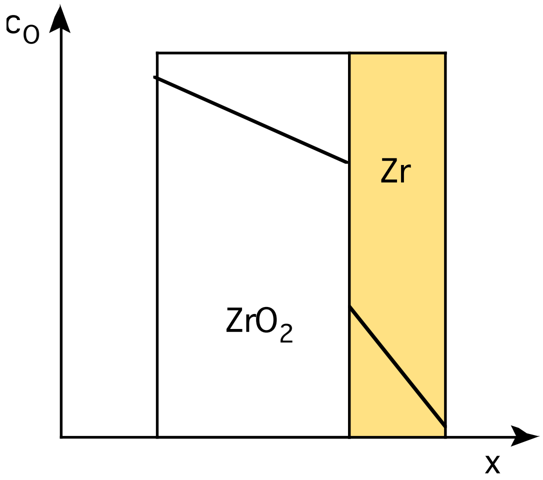
Diffusion and defects

Assume a thin foil of zirconium, heated to 1000K. On one side the foil is exposed to pure oxygen, on the other side to pure carbon monoxide (CO). The oxidation of Zr progresses as oxygen diffuses across the ZrO_2 layer. However, because Zr metal has a finite solubility for oxygen, the reaction at the ZrO_2/Zr interface is slowed down and comes to a halt before all Zr is oxidized.

a) Explain why.

b) What are the relative thicknesses of the ZrO_2 and Zr layers after very long time. Assume that the gas compositions on either side do not change.

For your explanations refer to the schematic below. The molecular weight of Zr is 91.22 g/mol, that of O is 16 g/mol. The density of ZrO_2 is 5.6 g/cm^3 and that of Zr is 6.49 g/cm^3. The concentration of oxygen in ZrO_2 at the ZrO_2/gas interface is 1.08 times higher than at the ZrO_2/Zr interface. The maximum solubility of oxygen in Zr is 2.5 mol%. The equilibrium concentration of oxygen in Zr at the Zr/CO(gas) interface is zero. The diffusion coefficients of O in ZrO_2 and Zr at that temperature are $2.3 \cdot 10^{-7}$ and $6.5 \cdot 10^{-6}$ cm^2/s respectively.



5.

A sphere of radius **R** composed of a porous catalyst is immersed in a solution. The solution contains a chemical at a concentration $\mathbf{c_0}$. This chemical diffuses into the catalyst at a diffusion rate **D**. Once inside the catalyst the chemical decomposes at a rate **r = -k c**.

a) Write down the transport equation needed to solve this problem and eliminate all unnecessary terms. Ignore end effects. Assume steady state. (2pts)

b) Write down the boundary conditions for this problem. (2pts)

c) Solve for the concentration of the chemical, **c**, as a function of radius. Simplify your answer in terms of hyperbolic functions (see box below). (2pts)

d) Detail the mathematical operations you would perform, given any expression for **c(r)**, to find the flux of chemical into the sphere and the total rate of chemical reacted in the catalyst per unit time? (DO NOT use your solution from part (c) in this part. Describe the operation generally.)(2pts)

e) Perform the calculation described in part (d) above. (2pts)

$$\sinh x = \tfrac{1}{2}\left(e^{x} - e^{-x}\right), \cosh x = \tfrac{1}{2}\left(e^{x} + e^{-x}\right), \tanh x = \sinh x / \cosh x$$

$$\frac{d \sinh u}{dx} = \left(\cosh u\right)\frac{du}{dx}, \frac{d \cosh u}{dx} = \left(\sinh u\right)\frac{du}{dx}$$

6.

Molecular effusion

Consider a cylindrical effusion reactor for the separation of hydrogen and deuterium. The reactor has a length L and a radius R. The walls of the container are porous with porosity ω. Assume (for simplicity) that H_2 and D_2 are present in equal proportions.

a) Derive and expression for the effusion rate of a gas with molecular weight m from the cylinder.

b) How long should you run the process to achieve maximal separation between the two isotopes, which is when the difference between the number of moles of H_2 and D_2 is largest?

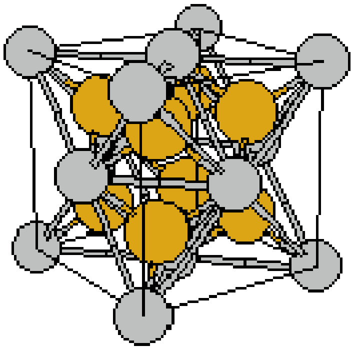
For expediency, please solve this problem using symbols rather that numerical values. Note that the average velocity of a gas particle is given by $\bar{v} = \sqrt{8RT/\pi m}$.

7.

<u>Structure Factor of Fluorite</u>: Derive simplified expressions for F^2 of fluorite, CaF_2. Determine the rules governing the observed reflections, and list the first 10 reflections that may be present. This crystal is FCC with a 3-atom basis

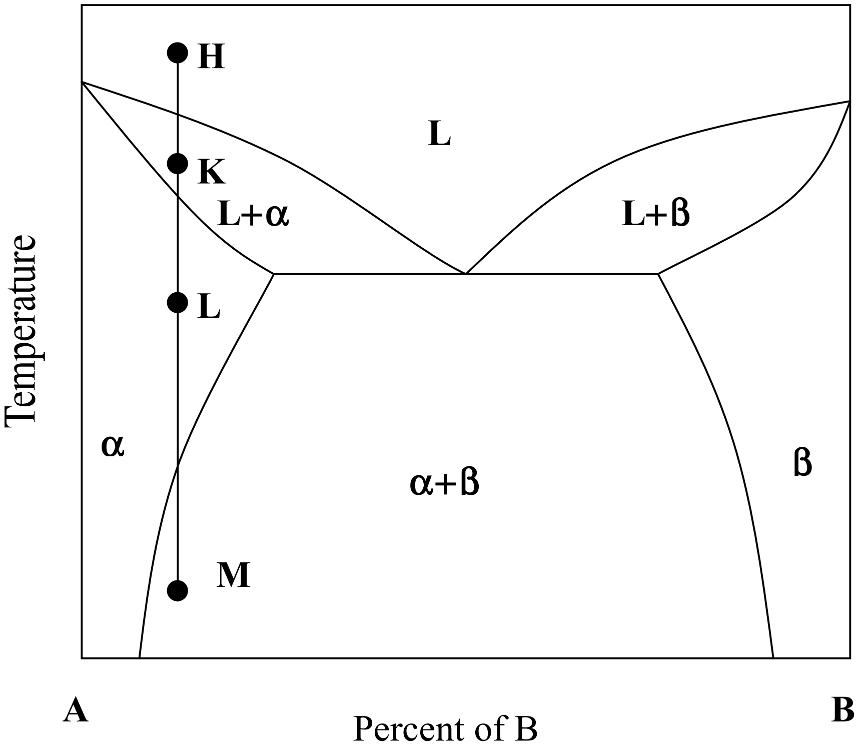
Ca: (0,0,0)

F: (1/4, 1/4, 1/4), (3/4, 3/4, 3/4)



8.

Figure 1 is a phase diagram of two metals A and B, which are partially soluble. Draw schematics and show the characteristics of powder x-ray diffraction patterns (ϑ–2ϑ) of the solid solutions at H, K, L, and M, respectively. Assuming the α phase has an f.c.c. structure with a = 0.4 nm, while the β phase has a b.c.c structure with a = 0.3nm.



Day 2 – STRUCTURE OF MATERIALS **CODE #________**

9.

The following schematic electron diffraction pattern of a single, isolated crystallite was obtained on a JEOL 4000 EX TEM operating at 350 kV. It is printed at 1:1 scale. The d-spacing of the planes corresponding to the Bragg spot indicated as spot 1 in the diagram was 0.8 nm.

a) What was the wavelength of the electrons?

b) What was the camera length L?

c) What was the camera constant (λ L)?

d) What are the d-spacings of the other two planes (2, 3) observed in the pattern?

e) Draw as accurately as possible the crystallite in real space, including the crystallographic planes corresponding to spots 1 and 3 and the overall size and shape of the crystallite itself.