Massachusetts Institute of Technology

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3.21 Kinetics Processes in Materials—Spring 2006

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9:30–10:55 A.M.

This is a *closed book* examination. Calculators may be used when necessary.

Please answer the questions directly on the exam pages. If you require more room, use the backs of the facing pages.

There are four questions on this examination, and each is worth 25 points. Apportion your time accordingly.

Keep your answers short and to the point. When appropriate, include sufficient information to indicate your reasoning. This will enable us to award appropriate credit even if you do not answer the question completely.

Good luck!

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Please write your name here

1. When equilibrated at high temperatures, f.c.c. magnesium oxide (MgO) will have equal numbers of negatively charged cation vacancies and positively charged anion vacancies uniformly distributed throughout the material. By answering the questions below, describe what will happen to the equilibrium cation and anion vacancy distributions if an MgO crystal is placed in a uniform electric field. Assume that the total numbers of both kinds of vacancies remains constant.

    (a) Write the general equations for the coupled forces and fluxes in this problem. Note any constraints on the coefficients in your equations.

    (b) What is an appropriate diffusion potential for the species in this problem? Explain how the diffusion potential could be used to characterize the steady state that would be obtained by annealing in an electric field for a very long time.

2. Interdiffusion in Au–Ni alloys occurs by the vacancy mechanism, and the intrinsic diffusivity of Au is always larger than that of Ni in this system. At 900°C, the interdiffusivity drops by about two orders of magnitude on going from pure Au to pure Ni. Suppose a one-dimensional diffusion couple was made up consisting of pure Au on the left and pure Ni on the right and that inert markers were placed at the interface prior to any interdiffusion. Then the diffusion couple was heated at 900°C for a long time to allow significant interdiffusion to occur.

   (a) Draw a schematic diagram illustrating the expected shape of the concentration of Ni vs. distance across the interdiffusion zone. Justify the shape of the curve you have drawn.

   (b) Which way would the inert markers placed at the original interface move as a result of the interdiffusion? By what mechanism would they move?

   (c) The lattice constants of Au and Ni are about 0.4 and 0.36 nm, respectively (both elements are f.c.c. and there is continuous solid solubility at 900°C). Would you expect the resulting atomic size difference to contribute to the marker motion? Explain your reasoning.

3. Consider a finite body $0 \leq x \leq 10$ μm with these initial and boundary conditions:

$$c(x, t = 0) \;=\; \begin{cases} c_0, & 1 \leq x \leq 2 \ \mu\text{m} \\ 0, & x < 1 \text{ and } x > 2 \ \mu\text{m} \end{cases} \tag{1}$$

$$J(x = 0, t) = J(x = 10 \ \mu\text{m}, t) = 0 \tag{2}$$

Assume a constant value of the interdiffusivity, $\tilde{D} = 10^{-16}\,\text{m}^2/\text{s}$.

(a) Superpose on a plot the initial concentration vs. distance profile and that which would be present at time $t = \infty$.

(b) Indicate how you would go about finding a solution for the time dependence of the resulting composition profile that would be valid for *all* times. *Note*: You should write down a few explanatory equations, but do not take time to work out the complete solution unless you have finished the remainder of the exam.

Problem 3, continued:

(c) Write down an approximate solution that will be valid for relatively "short" times by superposing two error-function solutions. Estimate the time interval over which you could be confident in using this solution.

(d) Another approximate solution could be obtained by using a single point source at $x = 1.5$ μm and a second "image" source at $x = -1.5$ μm. Would such a solution have any advantages over the error-function solution method suggested in part (c) above? Would it have any disadvantages?

4. Please identify which of the following statements is true or false. Give a brief justification for each answer. *Full credit requires concise, correct reasoning.*

(a) As consequence of the principle that local entropy production is nonnegative, the inter-diffusivity in binary alloys must be a positive quantity.

(b) For steady-state diffusion through a one-dimensional thin sheet with fixed concentrations at each end, the $c(x)$ profile inside the sheet could be concave up, linear, or concave down.

(c) For all crystalline materials it is possible to express the diffusion flux by the relation $\vec{J} = -\mathbf{D}\nabla c$ where the diffusivity $\mathbf{D}$ is a diagonal tensor (i.e., such that $D_{ij} = D_{ji} = 0$ when $i \neq j$).

(d) The vacancy diffusivity in a pure crystalline material, D_V, can be modeled by the relation $D_V = \Gamma r^2 \mathbf{f}/6$, with the correlation factor $\mathbf{f} = 1$.