3.205 Thermodynamics and Kinetics of Materials—Fall 2003

Kinetics Examination

December 8, 2003   10:00–11:30 A.M.

1. Answer these questions about Fick's laws of diffusion:

    (a) Write a general expression for Fick's first law and define all terms in the equation, and their dimensions.

    (b) Write a general expression for Fick's second law and explain its basis (i.e., where it comes from).

2. The solution to the diffusion equation for a point source of strength M (per unit length) located at the origin $x = 0$ in a one-dimensional system extending from $x = -\infty$ to $x = \infty$ is

$$c(x,t) = \frac{M}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \tag{1}$$

    (a) Use this solution to write an equation for the diffusion from a point source initially located at position $x = \Delta$ in a *semi-infinite* one-dimensional system extending from $x = 0$ to $x = \infty$.

    Hint: Solve this problem by superposing a second identical "image" point source of strength M located at position $x = -\Delta$ so that the symmetry plane at $x = 0$ will be a plane of zero flux. See Fig. 1 below.

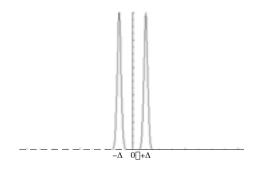   (b) Demonstrate that the solution you obtain from part (a) has zero flux at $x = 0$ for all times.

Figure 1: Image source at $x = -\Delta$.

3. The intrinsic point imperfections in potassium chloride, KCl, are Schottky defects that consist of charge-compensating cation and anion vacancies.

    (a) Write the formation reaction for a Schottky defect in KCl, using Kröger-Vink notation.

    (b) What specific point defects would you expect to be found in impure KCl that contained a small amount of $CaCl_2$?

    (c) Explain how the presence of $CaCl_2$ impurities in KCl might be apparent on an Arrhenius plot of cation diffusivity in KCl.

4. Martensitic transformations involve a shape deformation that is an invariant-plane strain (simple shear plus a strain normal to the plane of shear). The elastic coherency-strain energy associated with the shape change is often minimized if the martensite forms as thin plates lying in the plane of shear. Such a morphology can be approximated by an oblate spheroid with semiaxes (r, r, c), with $r \gg c$. The volume V and surface area S for an oblate spheroid are given by the relations:

$$V = \frac{4\pi}{3}r^2 c \text{ and } S = 2\pi r^2 \tag{2}$$

The coherency strain energy per unit volume transformed is given by

$$\Delta f_\varepsilon = \frac{Ac}{r} \tag{3}$$

(a) Find expressions for the size and shape parameters for a coherent critical nucleus of martensite. Use the data below to calculate values for these parameters.

(b) Find the expression for the activation barrier for the formation of a coherent critical nucleus of martensite. Use the data below to calculate the value of this quantity.

(c) Comment on the likelihood of coherent nucleation of martensite under these conditions.

Data

$\Delta f_B = -170 \text{ MJ/m}^3$ (chemical driving force at observed transformation temperature)

$\gamma = 150 \text{ mJ/m}^2$ (interphase boundary energy per unit area)

$A = 2.4 \times 10^3 \text{ MJ/m}^3$ (strain energy proportionality factor)

5. Use your knowledge of kinetic rate laws to answer the following:

(a) Annealing Alloy X, which is single-phase, for $2\,\text{hr}$ at $800\,\text{K}$ is found to increase the grain size from $25\,\mu\text{m}$ to $50\,\mu\text{m}$. Estimate the time required at $800\,\text{K}$ to increase the grain size from $50\,\mu\text{m}$ to $100\,\mu\text{m}$.

(b) Annealing Alloy Y, which contains a dispersion of spherical precipitates in a matrix, for $2\,\text{hr}$ at $800\,\text{K}$ is found to increase the average precipitate particle radius from $25\,\text{nm}$ to $50\,\text{nm}$. Estimate the time required to increase the average precipitate particle radius from $50\,\text{nm}$ to $100\,\text{nm}$. *State key assumptions you've made in arriving at your answer.*

6. Using concepts from nucleation and growth kinetics, explain why a time-temperature-transformation diagram consists of curves with a characteristic "C" shape.

Physical Constants

$$k_B = 1.38 \times 10^{-23} \text{ J/K (Boltzmann's constant)}$$
$$N_\circ = 6.023 \times 10^{23} \text{ (Avagadro's number)}$$