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3.21 Kinetics Processes in Materials—Spring 2006

Examination #2—Instructor's Solution

April 10, 2006

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!

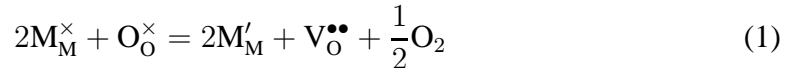
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Please write your name here

1. Consider an oxygen-deficient oxide  $\text{MO}_{3-x}$  that contains a low concentration of solute arising from the addition of the soluble oxide  $\text{AO}_2$ . Assume that oxygen diffusion occurs by a vacancy mechanism.

- (a) Write the reduction reaction for reducing  $\text{MO}_{3-x}$  and a corresponding equation for its equilibrium constant  $K^{\text{eq}}$ .

*Solution:* In a reduction reaction, oxygen will be liberated as a gas by giving up electrons which will reduce the charge on nearby cations. The liberated anion leaves an anion vacancy. The reduction reaction will have the form:



The corresponding equilibrium constant will be

$$K^{\text{eq}} = e^{-\Delta G/(kT)} = [\text{M}'_M]^2 [\text{V}_O^{\bullet\bullet}] P_{\text{O}_2}^{1/2} \quad (2)$$

- (b) Write a defect reaction for the incorporation of the solute A into  $\text{MO}_3$ .

*Solution.* M is hexavalent, A is tetravalent. Assume that A substitutes for M on cation sites. A reasonable incorporation reaction is:



- (c) Write the charge neutrality condition for the impure, nonstoichiometric oxide.

*Solution.* Assume Schottky defects to be the dominant intrinsic defects in  $\text{MO}_3$ . The charged species present will be cation vacancies, anion vacancies, impurity cations, and M ions that have captured one electron. The resulting charge neutrality condition is

$$[\text{M}'_M] + 2[\text{A}''_M] + 6[\text{V}_M^{\prime\prime\prime\prime}] = 2[\text{V}_O^{\bullet\bullet}] \quad (4)$$

- (d) Explain under what conditions it might be possible to use  $\text{MO}_3$  as the active component in an oxygen sensor.

*Solution.* The reduction reaction equilibrium constant depends on oxygen partial pressure, so an oxygen sensor must take advantage of the reduction regime. In this regime, it might be possible to relate electrical conductivity from the  $\text{M}'_M$  defects to oxygen partial pressure. To operate in this regime, the crystal must be sufficiently pure or the temperature must be high enough to avoid the extrinsic regime associated with any impurities. Also, the temperature must be sufficiently low to avoid the intrinsic regime. Note that reduction is favored at *low* oxygen partial pressures.

2. Harrison's "B regime" of short-circuit grain-boundary diffusion is illustrated in Fig. 1.

Consider a volume element in the boundary of dimensions  $\delta \times dy \times dz$  as shown in Fig. 2b. By relating the accumulation in the volume element to the fluxes into each of the six faces of

the volume element, show that the differential equation governing this regime has the general form

$$\frac{\partial c^B}{\partial t} = A \frac{\partial^2 c^B}{\partial y^2} + B \frac{\partial c^{XL}}{\partial x} \quad (5)$$

You do not have to evaluate the constants  $A$  and  $B$  in your derivation.

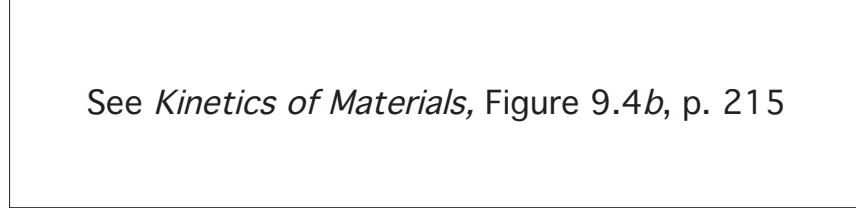


Figure 1: “B regime” of Short-Circuit Grain-Boundary Diffusion.

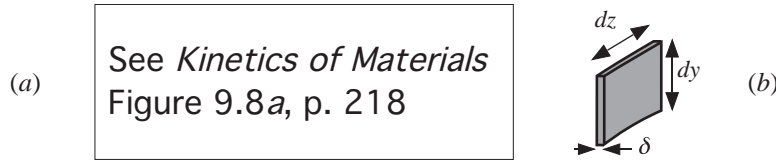


Figure 2: (a) Model Geometry for Diffusion Along a Grain Boundary. (b) Volume Element for Description of Short-Circuit Grain-Boundary Diffusion.

*Solution:* Assume that the concentration field is independent of  $z$  and that the concentration in the boundary  $c^B$  is independent of  $x$ . Consider the fluxes into and out of the volume element. Along the  $y$ -direction, material enters the volume element from the top and leaves at the bottom as solute is transported down the boundary. If the flux at the top of the volume element is  $J_y$ , at the bottom it will be  $J_y + dJ_y/dy dy$ . The contribution to the accumulation in the volume element from flow along  $y$  will be  $dJ_y/dy = D^B \partial^2 c_y^B / \partial y^2$ . The volume element will lose solute because of diffusion out of the grain boundary into the grain, and the accumulation will therefore be affected by diffusion into the grains along  $\pm x$ . The flux out of the boundary in the  $x$  direction is determined by the concentration gradient in the grain adjacent to the boundary, i.e. for  $x > 0$  the flux will be  $J_x = -D^{XL} dc^{XL}/dx$  and for  $x < 0$  the flux will be  $J_x = -D^{XL} dc^{XL}/dx$  as well. The total accumulation in the volume element will be

$$\frac{\partial c^B}{\partial t} dy dz \delta = -\frac{\partial J_y}{\partial y} dy dz \delta - J_x dy dz \quad (6)$$

or

$$\frac{\partial c^B}{\partial t} = D^B \frac{\partial^2 c^B}{\partial y^2} - \frac{D^{XL}}{\delta} \frac{\partial c^{XL}}{\partial x} \quad (7)$$

which has the desired form of Eq. 5.

3. The *Gibbs–Thomson* equation can be written in the form

$$\mu_B^\beta(P^\beta) - \mu_B^\beta(P^\alpha) = \frac{2\Omega_B \gamma}{r} \quad (8)$$

- (a) Explain the meaning of each quantity in this equation and give SI units for each quantity.

*Solution:*  $\mu_B^\beta(P^\beta)$  is the chemical potential of  $B$  atoms in the  $\beta$  phase at pressure  $P^\beta$ , and units are J/atom.  $\mu_B^\beta(P^\alpha)$  is the chemical potential of  $B$  atoms in the  $\beta$  phase at pressure  $P^\alpha$ , and units are J/atom.  $\Omega_B$  is the atomic volume of species  $B$ , and units are  $\text{m}^3$ .  $\gamma$  is the excess free energy per unit area of an  $\alpha/\beta$  interface, and units are  $\text{J}/\text{m}^2$ .  $r$  is the radius of a spherical particle of  $\beta$  phase, with units of m.

The Gibbs–Thomson equation indicates how the chemical potential of a species in a two-phase system at equilibrium changes with curvature of the  $\alpha/\beta$  interface. For a spherical fluid solution with a spherical particle of  $\beta$  in an  $\alpha$  matrix, the equation indicates how  $\mu_B$  changes with  $r$ , compared to a system in which the  $\alpha/\beta$  interface is flat.

- (b) Explain the relevance of the Gibbs–Thomson equation to the phenomenon of particle coarsening (Ostwald ripening).

*Solution:* Ostwald ripening occurs in a two-phase system consisting of a matrix phase and particles of an embedded second phase. The Gibbs–Thomson equation indicates that the solubility of solute in the matrix phase will depend on particle radius such that the solubility in a system with small particles will be greater than that in a system with particles having larger radii. Assuming local equilibrium at the particle/matrix interfaces in a system with a distribution of particle radii, concentration gradients result in the matrix phase such that solute will diffuse from small particles to large particles. This results in a gradual shift of the particle size distribution to larger sizes.

- (c) The accompanying figure shows coarsening data from Hardy and Voorhees’ experiments on semi-solid Pb–Sn alloys. In what way are the data *consistent* with a prediction of the mean-field theory of particle coarsening? In what way are the data *inconsistent* with the mean-field theory?

See *Kinetics of Materials*, Figure 15.9, p. 372

Figure 3: Coarsening Data on Semi-Solid Pb–Sn Alloys (Hardy and Voorhees 1988).

*Solution.* The plot is effectively  $\langle R \rangle^3$  vs.  $t$  and the data for each volume fraction fall on a straight line. Hence the results are consistent with the “t-to-the-one-third” law prediction of the mean-field theory. However, the mean-field theory does not consider a particle volume fraction effect (in fact, it is strictly valid in the limit of zero volume fraction of particles), but the data clearly show that the rate constant for coarsening is an increasing function of particle volume fraction.

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) In KCl containing  $\text{MgCl}_2$ , there will be an intrinsic regime of cation diffusion in which the cation vacancy concentration is independent of temperature.

*Solution.* FALSE. The intrinsic regime will have a defect population that obeys an Arrhenius law. In this impure material the extrinsic regime will have a cation defect population that is independent of temperature.

- (b) The activation volume for self-diffusion in metallic glasses is near zero, indicating that self-diffusion likely takes by a cooperative many-body process.

*Solution.* TRUE. The activation volume is determined from the pressure dependence of the diffusivity. The very small activation volume observed in self-diffusion in metallic glasses indicates that defects like vacancies or interstitials that have excess volume likely do not play a role in diffusion. A cooperative process is consistent with a very small activation volume.

- (c) The theory of random walks can be used to model self-diffusion in a polymer melt.

*Solution.* TRUE. The reptation model for self-diffusion in a long-chain polymer melt involves the concept of reptation time during which a given polymer molecule remains attached to its primitive tube. During one reptation time interval the molecule's center of mass executes a random walk related to the root mean square end-to-end length of the molecule.

- (d) Single-phase interfaces tend to migrate toward their center of curvature.

*Solution.* TRUE. Motion of an interface normal to itself results in an area change if the interface has non-zero mean curvature. Migration toward the center of (mean) curvature guarantees that the interface area will decrease.