MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Kinetic Processes in Materials

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Exam 2: Handed out 9 April; due by 5PM, 12 April, in 13-5026

Note to students: This exam is take-home and open reference. You may not consult classmates or other people for assistance on the exam. The exams will be graded comparatively—that is, your answers will be judged on the basis of their accuracy, thoroughness, clarity of expression, physical insight, and presentation. Be careful to state important assumptions or important limitations of your solutions.

A concise answer is preferable to a long answer with the same content.

Question 2.1

A computer simulation of diffusion via the vacancy mechanism is performed on a square lattice of screen pixels with a spacing of $a = 0.5$ mm. The computer performs the calculations so the the vacancy jumps at a constant rate of $\Gamma = 1000\text{s}^{-1}$. The simulation cell is a square of edge length 5 cm, containing 10,000 pixels. There is just one vacancy in the simulation cell, and as it moves, by nearest-neighbor jumps, it remains within the cell (by using periodic boundary conditions or reflection at the borders).

2-1-a Estimate the *vacancy diffusion coefficient* in this simulation if the vacancy moves by a random walk. Estimate the average *time* that it would take for the vacancy to move from the center of the cell to the cell border.

2-1-b One "tracer" atom, represented by a specially marked pixel, is initially located at the center of the simulation cell. The vacancy is introduced in the cell at a random location, and then moves by a random walk. Estimate the value of the *tracer diffusion coefficient* in this simulation. Estimate the average *time* that it would take for the tracer atom to move from the center of the cell to the cell border.

Question 2.2

Several different diffusion mechanisms have been discussed in lecture, including:

2-2-a Ring mechanisms

2-2-b Vacancy mechanisms

2-2-c Interstitialcy Mechanisms

2-2-d Interstitial Mechanisms

2-2-e 'Activated volume' mechanisms in glasses

2-2-f Diffusion of isolated polymer chains in solution

2-2-g Diffusion in dense polymer systems by reptation.

Pick any two of the above mechanisms and consider the hydrostatic pressure dependence of the associated diffusion coefficients.

Find and report data from published literature that illustrate pressure dependence for these two mechanisms. Describe the experiments used to obtain the data.

Rationalize the observed pressure dependence of the diffusivity in terms of the operative diffusion mechanisms.

Question 2.3

A certain company uses a CVD process to produce tantalum thin-film coatings as diffusion barriers against nitrogen influx. Nitrogen diffuses interstitially in tantalum and the diffusion constant is $D_{\mathrm{N}}^{\mathrm{Ta}} = D_0^{\mathrm{Ta}} \exp[-Q_{\mathrm{Ta}}/kT]$ where $D_0^{\mathrm{Ta}} = 5.5 \times 10^{-7}\mathrm{m}^2/\mathrm{s}$ and $Q_{\mathrm{Ta}} = 2.63 \times 10^{-19}\mathrm{J/atom}$.

It is suggested that the same effective diffusion barrier can be obtained by a two-step CVD process in which a composite film of iron and tantalum is produced at a considerable savings in materials costs because iron can be obtained for about $100/ton whereas tantulum costs about $400/pound.

Nitrogen diffuses interstitially in Fe with a temperature-dependent diffusion constant given by $D_{\mathrm{N}}^{\mathrm{Fe}} = D_0^{\mathrm{Fe}} \exp[-Q_{\mathrm{Fe}}/kT]$ where $D_0^{\mathrm{Fe}} = 3.0 \times 10^{-7}\mathrm{m}^2/\mathrm{s}$ and $Q_{\mathrm{Fe}} = 1.26 \times 10^{-19}\mathrm{J/atom}$.

Design and processing constraints specify that the overall thickness of the diffusion barrier cannot increase more than a factor of two.

Considering only material costs, analyze the economic benefits of the composite diffusion barrier.

Question 2.4

The accompanying figure provides data for the sodium ion diffusivity in NaCl containing a small amount of $CdCl_2$.

2-4-a Write a defect incorporation reaction for $CdCl_2$.

2-4-b Write expressions for the diffusion coefficient of sodium in the intrinsic and extrinsic regimes shown in the data.

2-4-c Determine the activation energy for vacancy migration and the Schottky defect formation enthalpy from the data.

2-4-d Estimate the concentration of Cd in this sample (in units of g/cm^{-3}).

2-4-e If the only impurity present in NaCl was KCl, in what ways would you expect the data shown in the figure to differ? Explain your answer.