Problem set 7
Homework Set 7 is due 5:00 pm, Mar 27. Please keep a copy to check it against the correct solutions. Solutions will be posted on Mar 28, and your corrections are due 5:00 pm, April 3.
Reading: Cussler, Chapter 16 (review) and Chapter 17 (preview)

Problem 1. Surface electrochemical reaction of Fe^{2+}
Information:
As part of a study of electrochemical kinetics, a gold electrode was inserted into a solution containing sulfuric acid and small amounts of ferrous ion. Potential was applied between the electrode and the second reversible electrode. At the gold the iron is oxidized as \( \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \). The current density \( i(\text{amp/cm}^2) \) was measured under a fixed potential, and the correlation is \( \frac{c_1}{t} = 2.5 + 50t^{0.5} \). Here \( c_1 \) is the ferrous concentration in moles per liter and \( t \) is the time in minutes.

Questions:
(a) Find the expression for \( c_1/j_1 \) (Hints: read notes for “Electrochemical cell.”)
(b) Find the expression for \( c_1/j_1 \) from the given \( c_1/i \) correlation, using \( j_1 \) (mol/cm²-s) = \( i \) (A/cm²)/(96500 A-s/mol)
(c) Compare (a) with (b), calculate the rate constant of the surface reaction (4.15*10⁻³ cm/s) and the diffusion coefficient of the ferrous ion (Ans. 8.1*10⁻⁶ cm²/s).

Problem 2. Growing of a KCl crystal
Information:
A spherical potassium chloride crystal with 0.05 cm in diameter is immersed in a 10% supersaturated (110% \( c^{\text{sat}} \)) aqueous solution containing about 25 wt% potassium chloride. The crystal is growing at a rate of 0.002 cm/min. The solution flows pass the crystal at 6 cm/sec. The solution’s viscosity and density are 1.05 cp and 1.2 g/cm³, and the crystal’s density is 1.984 g/cm³.

Questions:
(a) Calculate the mass transfer coefficient by the correlation of the forced flow around a sphere. Use 1.944*10⁻⁵ cm²/s for diffusion coefficient of potassium chloride in water. (Ans. 0.011 cm/s)
(b) Determine the contribution of diffusion limitation into the rate of crystal growth, by calculating the ratio of the diffusion resistance to the total resistance. (Ans. 22.2%)

Problem 3. Cu-Si reaction
Information:
When copper and silicon are placed together, a layer of CuSi grows at the interface. The thickness of this layer at 350 °C is \( l = (1.41 \times 10^{-4} \text{cm/sec}^{0.5}) \times t^{0.5} \). The layer is formed by the reaction of Cu at the Cu₃Si-Si interface. The reaction is controlled by the diffusion of Cu through Cu₃Si.

Questions:
(a) Show that the variation of thickness versus time is consistent with a diffusion mechanism.
(b) Discuss what reaction stoichiometry would be required to produce this same variation.
(c) Calculate the diffusion coefficient (Ans. 1.47*10⁻¹⁰ cm²/s) and compare it with other values for diffusion in solids. In this experiment, the driving force of Cu₃Si is believed to be 1.5 mol% Cu
Problem 4. Air hydrate

Information:
Ancient air is trapped in bubbles deep within polar ice. The bubbles get fewer and smaller as the depth of ice gets deeper. These decreases are the results of the formation of an air hydrate phase. However, both bubbles and air hydrate coexist, even when only the hydrate phase is expected to form. P. B. Price (Science, 267, 1802 (1995)) explains this by postulating a layer of air hydrate around each bubble. To form more hydrate, water must diffuse through the hydrate to the inner surface of the bubble; the diffusion coefficient for this process is

\[ D = 2000 \frac{cm^2}{sec} \times \exp\left(-0.90 \frac{ev}{k_B T}\right) \]

As water reaches the inner surface of the hydrate, it reacts to form more hydrate, so the resistance to water diffusion increases with time.

Questions:
(a) Estimate the time to react all the air at -46°C (the temperature of South Pole ice) in a 0.02 centimeter bubble of air at 1 atmosphere. (1\times10^5 years)
(b) Repeat the estimation for a 0.20 centimeter bubble. (1\times10^7 years)

* Assume density of hydrate and water is equaled.
* Boltzmann constant \( k_B = 8.617 \times 10^{-5} \text{ ev-K}^{-1} \)
* Use the equation for diffusion through a spherical shell (see notes).

Premium problem. Heterogeneous reforming reaction

Following the notes in class, derive the kinetic equation for diffusion limited irreversible reforming reaction at the surface of type \( vA_1 \rightarrow A_2 \) with the reaction rate \( k_2^+ \) and diffusion coefficient \( D \). Assume the film model for external diffusion with the boundary condition \( c_1 = c_{1,0} \) at \( z=0 \) and the surface of reaction placed at \( z=l \). Account for reaction-induced convection. Explore the limiting case of the very fast reaction.