3.185 Problem Set 3

More diffusion

Due Friday September 26, 2003

1. W^3C Problem 27.16. (15)

2. A thin metal foil is used to separate hydrogen from other gases with lower diffusivity in the metal. (17)
   Combining principles of thermodynamics and diffusion, one can write the flux of a diatomic gas such as hydrogen through a foil as:
   $$J = -\frac{P_0^* e^{-Q_p/RT}}{\delta}\left(\sqrt{p_1} - \sqrt{p_2}\right),$$
   where P_0^* and Q_p are properties of the material, δ the thickness of the foil, and p_1 and p_2 the gas partial pressures on the two sides of the foil. The table below gives values of P_0^* and Q_p for hydrogen diffusing in nickel, copper and aluminum:

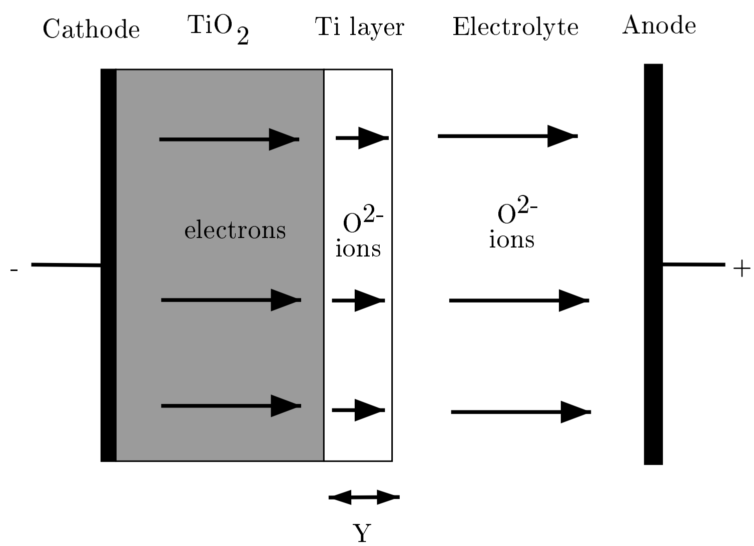
Metal	P_0^*, $\frac{\text{cm}^3\text{(STP)}}{\text{s}\cdot\text{cm}\sqrt{\text{atm}}}$	Q_p, $\frac{\text{cal}}{\text{mol}}$
Nickel	1.2×10^{-3}	13850
Copper	1.9×10^{-4}	17350
Aluminum	0.37	30800

   (a) The metal foil is 0.2 mm thick, and H_2 partial pressure is 0.2 atm on the hydrogen-rich side. If the temperature is 400°C and there is negligible hydrogen on the other side (since it's being pumped away), calculate the flux of hydrogen through the foil in cubic centimeters at STP per unit area per second for nickel, copper and aluminum. (12)

   (b) At what hydrogen partial presure (on the H_2-rich side) will the flux be half of what you calculated in part 2a? Briefly explain the flux/pressure scaling in terms of thermodynamics and/or kinetics. (5)

3. The FFC-Cambridge process for titanium reduction (23)

The FFC-Cambridge process for producing titanium (invented at Cambridge University, as some of you will be happy to know) involves electrochemically diffusing oxide ions out of titanium oxide, leaving behind a layer of porous titanium metal, as shown below.



FFC-Cambridge process, shown in planar geometry for simplicity (the real process uses an approximately cylindrical geometry with the electrode at the center).

We're going to ignore the electrochemistry for now, and focus on the reaction and diffusion. We'll measure x from the outer surface of the titanium layer (away from the TiO_2). Assume $C_{O^{2-}} = 0$ there at $x = 0$, and we'll call the O^{2-} concentration C_i in the porous titanium next to the Ti-TiO_2 interface. The process is limited by either:

- quasi-steady-state diffusion of oxide ions through the porous titanium layer of thickness Y, or
- the charge transfer reaction at the Ti-TiO_2 interface:

$$\mathrm{TiO_2} + 4\mathrm{e}^- \Rightarrow \mathrm{Ti} + 2\mathrm{O}^{2-}.$$

  We'll treat the net reaction rate as proportional to the difference between maximum oxide ion solubility in the titanium C_{eq} and actual oxide ion concentration in the titanium at the interface C_i (to account for the back-reaction):

$$J_O = k(C_{eq} - C_i).$$

(a) Give the name and the form of the dimensionless number that indicates which mechanism limits the process. When this number is large, is the process reaction-limited or diffusion-limited? (6)

(b) Sketch the oxygen concentration as a function of x in the porous titanium layer and TiO_2 layer (it won't vary across the TiO_2 layer), for small and large values of the dimensionless number from part 3a. (8)

(c) Write an expression for the diffusion flux through the porous titanium layer. (4)

(d) Sketch the relationship between layer thickness Y and time t as the layer grows, showing a transition between reaction-limited and diffusion-limited operation. (5)

4. Iron oxidation (15)

The mass of oxygen absorbed per unit area during metal oxidation can be calculated by the following equation:

$$\left(\frac{\Delta m}{A}\right)^2 = k_p t,$$

where k_p is a material property having to do with diffusivity and oxide thickness as given in this table for various metals:

Metal	Oxide	k_p, (kg O_2)^{2}m^{-4}s^{-1}	Temp., °C	p_{O_2}, atm
Co	CoO	2.43×10^{-6}	1000	1.0
Cu	Cu_2O	6.3×10^{-7}	1000	0.083
Ni	NiO	3.8×10^{-8}	1000	1.0
Fe	FeO	1.6×10^{-5}	1000	3×10^{-14}
Fe	$FeO/Fe_3O_4/Fe_2O_3$	1.4×10^{-4}	1000	1.0
Ni-10%Cr	Complex	5.0×10^{-8}	1000	1.0
Cr	Cr_2O_3	1.3×10^{-9}	900	0.1
Fe-1%Ti	Complex	1.6×10^{-5}	1000	1.0
Al	Al_2O_3	8.5×10^{-14}	600	1.0

A thick iron slab is heated to 1000°C to prepare it for rolling into plate form. It spends about 30 minutes at that temperature, and assume it is cooled very quickly during rolling.

(a) Using the table above, calculate the approximate mass of iron oxides per unit area before rolling. Assuming most of this is Fe_2O_3 with density $\rho = 5.24\frac{\text{g}}{\text{cm}^3}$, calculate the approximate thickness of the oxide layer. (10)

(b) If 1% titanium is added to the iron, how does this change your answer to part 4a? (Compare weight gain, not thickness, since you'd need the density of the resulting oxide to determine thickness.) (5)

5. Dimensional Analysis: the Shrinking Gaussian (30)

A very thin zinc coating of thickness δ is diffusing into a thick (relative to the coating) sheet of steel to make a zinc-iron alloy. As discussed in class, for long times, the solution to the time-dependent diffusion equation is the "Shrinking Gaussian":

$$C = \frac{\beta}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

where β is the product of initial concentration of zinc in the coating and coating thickness. Assume that zinc and iron are completely miscible with a uniform diffusion coefficient throughout.

(a) Write all of the units of all of the dimensions involved (*e.g.* C, β, x, etc.). (5)

(b) Write the number of dimensions and the number of base units, and use the Buckingham pi theorem to determine the number of dimensionless parameters. (6)

(c) Construct your dimensionless parameters, keeping at least the concentration C and distance from the center x, and eliminating as many others as possible. (8)

Note: you *may* have square roots, *i.e.* exponents which are multiples of $\frac{1}{2}$, not just integers.

(d) Rewrite the Shrinking Gaussian solution above in terms of your new dimensionless parameters, *i.e.* $\pi_C = ...$ Include all coefficients in all parts of the Shrinking Gaussian. (6)

(e) Draw a graph of this dimensionless solution, labeling the maximum dimensionless concentration and the width. (5)