Assignment #3: Thermodynamics & Deposition

(due to Wednesday, February 27, 2017)

1) You are involved in deposition ZnS and CdS films for infrared optical coatings. Thermodynamic data reveal:

1. $$H_2S\,(g) + Zn(g) \rightarrow ZnS\,(s) + H_2\,(g)$$
$$\Delta G^0 = -76{,}400 + 82.1\cdot T - 5.9\cdot T\cdot \ln T \qquad (cal/mol)$$

3. $$H_2S\,(g) + Cd(g) \rightarrow CdS\,(s) + H_2\,(g)$$
$$\Delta G^0 = -50{,}000 + 82.2\cdot T - 6.64\cdot T\cdot \ln T \qquad (cal/mol)$$

a. Are these reactions endothermic or exothermic?
b. In practice, reactions 1 and 2 are carried out at 680°C and 600°C, respectively. From the vapor pressures of Zn and Cd at these temperatures, estimate the P_{H_2S} / P_{H_2} ratio for each reaction, assuming equilibrium conditions.

partial pressure of Zinc is given via $\log(p) = -\frac{7070}{T} + 9.41$ (T in K; p in mmHg)

partial pressure of Cadmium is given via $\log(p) = -\frac{5940}{T} + 9.02$ (T in K; p in mmHg)

A. C. Egerton, Vapor Pressure of Zinc, Cadmium and Mercury; Phil. Mag., Vol. 33, p. 33, 1917

2) Epitaxial deposition of Si can be achieved by disproportionation reaction

$$Si + SiCl_4 \leftrightarrow 2SiCl_2 \qquad \left[\Delta G^\circ = 83{,}000 + 3.64\cdot T\cdot \ln T - 89.4T \text{ (cal/mol)}\right]$$

The reaction is carried out in a closed long tubular atmospheric pressure reactor whose diameter is 15 cm. Deposition of Si occurs on a substrate maintained at 750°C and located 25 cm away from the source, which is heated to 900°C.

a. Assuming that the thermodynamic equilibrium prevails at the source and substrate, calculate the flux of $SiCl_2$ transported to the substrate if the gas viscosity is 0.8 mPoise. [Hint: You may assume a linear pressure drop between the source and substrate].
b. Consider the same reactor in which one-dimensional steady-state diffusion and convection processes occur together with a homogeneous first-order chemical reaction (not pure viscous flow as previous question). Assume the concentration *C(x)* of a given species satisfies the ordinary differential equation

$$D\cdot\frac{d^2C}{dx^2} - v\cdot\frac{dC}{dx} - K\cdot C = 0,$$

where K is the chemical rate constant and x is the distance along the reactor. If the boundary conditions are C(x=0) = 1 and C(x=1 m) = 0 derive an expression for C(x). Plot this expression for the concentration profiles if D = 1000 cm^2/s, v = 100 cm/s, and K=1 s^{-1}. What is the flux at 25 cm away from the source (C(x=0))?