Problem 1. (4 points) chapter 14
A recent paper reported use of a laser beam to increase the rate of crystal nucleation. (Nasirin Mirsaleh-Kohan, et al., Laser Shock Wave Induced Crystallization, Cryst. Growth Des., 2017, 17 (2), pp 576–581, DOI: 10.1021/acs.cgd.6b01437: This paper is readily accessible through the UMD library.) A laser pulse locally increased temperature and pressure, apparently increasing the rate of crystal nucleation. Recall Kondepudi’s equation 14.5.8 for the rate of nucleation:

\[ J = J_0 e^{-\frac{16\pi y^3 V_m^2}{3 k_B T} \frac{\Delta \mu^2}{\Delta T}} \]

a) Show that \( \Delta \mu(P_0 + \delta P, T_0 + \delta T) = \Delta \mu(P_0, T_0) + \Delta V_m \delta P - \Delta S_m \delta T \).
State the (or your) definition of \( \Delta \mu, \Delta V_m, \) and \( \Delta S_m \).
b) The authors state that \( \Delta V_m, \) and \( \Delta S_m \) are positive. Explain briefly.
c) Supersaturation, \( S \), is the ratio of the solute's concentration to its solubility: \( S = \frac{c}{c_0} \). The following connection is common: \( \Delta \mu(P_0, T_0) = RT \ln S \). Justify or derive that connection.
d) Suppose the solution is initially at temperature \( T_0 \), where \( S \) is known. A laser pulse raises \( T \) to \( (T_0 + \delta T) \) and \( P \) to \( P_0 + \delta P \). Starting with Kondepudi's equation 14.5.8 (above) and using parts a and c above, show that

\[ J = J_0 e^{-\frac{16\pi y^3 V_m^2}{3 k_B (T_0 + \delta T)(RT_0 \ln S + \Delta V_m \delta P - \Delta S_m \delta T)^2}} \]
e) The initial-pressure, initial-temperature rate is \( J_{0,0} \).

\[ J_{0,0} = J_0 e^{-\frac{16\pi y^3 V_m^2}{3 k_B (T_0 + \delta T)(RT_0 \ln S)^2}} \]

The ratio \( J/J_{0,0} \) can be calculated without knowing the initial-condition rate \( J_0 \).
Values for NaCl nucleation: \( y=0.060 \text{ J/m}^2, V_m=2.7 \times 10^{-5} \text{ m}^3/\text{mol}, \)
\( \Delta V_m=2.0 \times 10^{-5} \text{ m}^3/\text{mol}, \Delta S_m=10 \text{ J/mol} \cdot \text{K}. \)
Suppose \( T_0=298 \text{ K and } \delta T=10 \text{ K.} \) Let \( S=1.4 \). Graph \( \log_{10}(J/J_{0,0}) \) versus \( \delta P \) from 0 to 10 MPa.
**Problem 2** (4 points) chapter 15.

Consider the reaction of A to B through an intermediate, I. A, B and I are dissolved in water. All solutions may be considered ideal, so \( \mu_A = \mu_A^0 + k_B T \ln ([A]) \), for example. For simplicity, "A" can stand for either the reactant or its molar concentration. Likewise, B and I. The cross-sectional area of each cell end is 0.80 mm\(^2\).

The chemical reaction mechanism has four steps: two forward, two reverse. All steps are first-order. All steps have the same rate coefficient, \( k \). Let \( k = 10.0 \text{ s}^{-1} \).

The reactions occur inside a cell. The cell is thermostatted. Everywhere, temperature is the same. The coordinate "\( z \)" runs along the cell.

From external reservoirs, A is supplied at the left and removed at the right. B is supplied at the right and removed at the left.

Values for NaCl nucleation:
- \( \gamma = 0.060 \text{ J/m}^2 \),
- \( V_m = 2.7 \times 10^{-5} \text{ m}^{-3} \),
- \( \Delta V_m = 2.0 \times 10^{-5} \text{ m}^3/\text{mol} \),
- \( \Delta S_m = 10 \text{ J/mol} \cdot \text{K} \).

Suppose \( T_0 = 298 \text{ K} \) and \( \delta T = 10 \text{ K} \). Let \( S = 1.4 \). Graph \( \log_{10}(J/J_{0,0}) \) versus \( \delta P \) from 0 to 10 MPa.ft.

Given: \( A = 0.1 \text{ M} - 0.025 \text{ M/mm} \times z \), \( B = 0.05 \text{ M} + 0.025 \text{ M/mm} \times z \), \( I = 0.01 \text{ M} \) at all \( z \). \( T = 293 \text{ K} \).

(a) If the system were at equilibrium, what would be the value of \( I/A \) ?

(b) The system is driven by supply and removal of A and B, so it cannot be at equilibrium but could be at steady state. Is \( dI/dt = 0 \), for the given concentrations?

(c) Use equation 15.5.12 to calculate (write an equation for) the entropy production, \( \sigma \).

Notes:
- Let us take \( J_A = J_B = J_I = 0 \).
- There is no external potential: \( \psi = 0 \).
- Affinity and reaction rate expressions are in chapter 16. For this problem's two reactions \( A_1 = RT \ln \left( \frac{A}{I} \right) \), \( A_2 = RT \ln \left( \frac{I}{B} \right) \), \( v_1 = k (A - I) \), \( v_2 = k (I - B) \). (\( R \) instead of \( k_B \) so if concentrations are converted to mol/m\(^3\), \( \sigma \) will be in units of J/(m\(^3\)-K-s)).

(d) Graph \( \sigma \) as a function of \( z \).

(e) Use your \( \sigma \) formula to calculate \( dS/dt \) (equation 15.2.4).