

Exam II Practice Problem Solutions 580.241

1. a) For a t state system, what distribution (p_1, p_2, \dots, p_t) has maximum entropy, and what is S_{\max} ?

$$\text{max: } p_i = \frac{1}{t}, \quad S_{\max} = k \ln t$$

$$\text{min: } p_i = 1 \text{ for some } i, \quad p_{j \neq i} = 0, \quad S_{\min} = 0$$

b) What constraint must always be satisfied by the distribution (p_1, p_2, \dots, p_t) ?

$$\sum_{i=1}^t p_i = 1$$

c) Use the technique of Lagrange multipliers to show that your distribution in 1a) maximizes the entropy, S , under the constraint in b).

$$S(p_1, p_2, \dots, p_t) = -k \sum_{i=1}^t p_i \ln p_i \qquad g(p_1, p_2, \dots, p_t) = \sum_{i=1}^t p_i = 1$$

$$\text{LM: } \frac{\partial S}{\partial p_i} - \alpha \frac{\partial g}{\partial p_i} = 0 \quad \text{for all } i$$

$$\frac{\partial S}{\partial p_i} = -k(1 + \ln p_i) \qquad \frac{\partial g}{\partial p_i} = 1 \qquad p_i = e^{-1-\alpha/k} \quad \text{eliminate } \alpha \text{ by dividing by } \sum_{i=1}^t p_i = 1$$

$$\rightarrow p_i = \frac{e^{-1-\alpha/k}}{\sum_{i=1}^t e^{-1-\alpha/k}} = \frac{e^{-1-\alpha/k}}{t e^{-1-\alpha/k}} = \frac{1}{t}$$

2. General

a) For a one-component system, give four precise mathematical definitions of the chemical potential.

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} = \left(\frac{\partial F}{\partial N} \right)_{V,T} = \left(\frac{\partial H}{\partial N} \right)_{S,V} = \left(\frac{\partial G}{\partial N} \right)_{T,p} = T \left(\frac{\partial S}{\partial N} \right)_{U,V}$$

b) Dissolving salt in water is endothermic, which means $\Delta h_{\text{solution}} = h_{\text{mixed}} - h_{\text{unmixed}} > 0$. If the system is defined to be the salt plus the water, when the salt dissolves, does the entropy of the system increase or decrease or stay the same? Does the entropy of the outside world increase or decrease or stay the same?

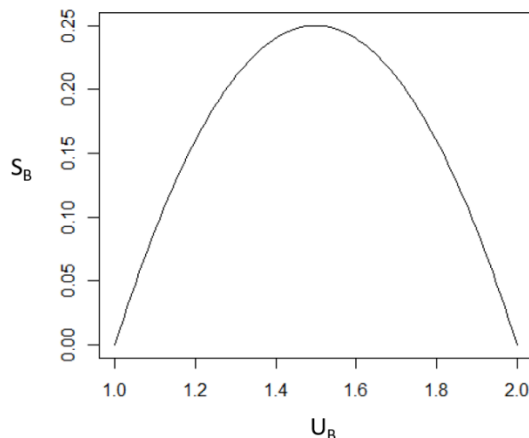
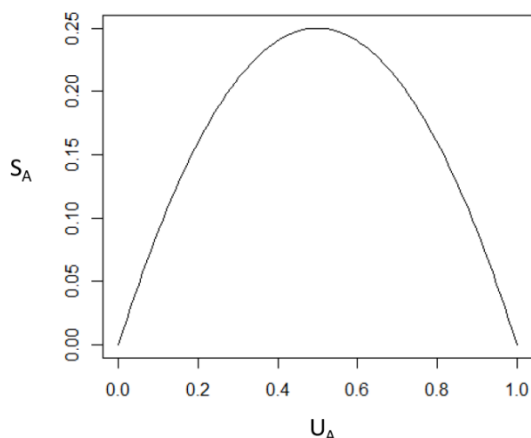
System entropy increases.

Since $\Delta h > 0$, system absorbs heat from outside world at fixed T , so entropy of outside world decreases.

c) T or F Sometimes the entropy of a macroscopic system can spontaneously decrease, but only for a very short time, and only by a very small amount.

True.

3. Two of your classmates have discovered systems that when isolated have parabolic entropy functions $S(U)=(U-U_{\min})(U_{\max}-U)$, $U \in [U_{\min}, U_{\max}]$. They create 2 systems, A and B, where $U_{A,\min}=0$, $U_{A,\max}=1$, and $U_{B,\min}=1$, and $U_{B,\max}=2$, and then thermally isolate each system and transfer energy to each system until $S_A=S_A(U_A)$ and $S_B=S_B(U_B)$. Then the two systems are brought into thermal contact and energy flows between system A and system B until they come into thermodynamic equilibrium with each other, but they are still isolated from the outside world.



a) 5pts. If initially $U_A=3/5$ and $U_B=6/5$, what are $U_{A,\text{final}}$ and $U_{B,\text{final}}$ after A and B are brought into thermal contact?

$U_{\text{total}} = 9/5$, at equil $T_A=T_B \rightarrow U_B=1+U_A \rightarrow U_{A,\text{final}}=2/5$, $U_{B,\text{final}}=7/5$

b) 5pts. If initially $U_A=3/5$ and $U_B=6/5$, after coming into thermodynamic equilibrium, what are the signs of T_A and T_B ?

$T_A, T_B > 0$

c) 5pts. If initially $U_A=4/5$ and $U_B=7/5$, what are $U_{A,\text{final}}$ and $U_{B,\text{final}}$ after A and B are brought into thermal contact?

$U_{\text{total}} = 11/5$, at equil $T_A=T_B \rightarrow U_B=1+U_A \rightarrow U_{A,\text{final}}=3/5$, $U_{B,\text{final}}=8/5$

d) 5pts. If initially $U_A=4/5$ and $U_B=7/5$, after coming into thermodynamic equilibrium, what are the signs of T_A and T_B ?

$T_A, T_B < 0$

e) 5pts. Does energy always flow from the high energy system into the low energy system?

No

f) 5pts. Find an initial U_A and U_B such that after A and B are brought into thermal contact both T_A and T_B will be either $\pm \infty$, but before being brought into thermal contact T_A and T_B are different.

$U_{A,\text{initial}}=1/5$, $U_{B,\text{initial}}=9/5$. Anything with $U_{A,\text{initial}}+U_{B,\text{initial}}=2$ and $U_{A,\text{initial}} \neq 1/2$ will work.

4. Consider a molecule with two energy states, the higher energy state has an unknown number of microstates, W_1 , and an unknown energy, ε_1 . You are trying to determine W_1 , and ε_1 from measurements of the specific heat C_V . Consider a collection of N distinguishable molecules in equilibrium with a temperature bath at fixed T and V .

_____ $\varepsilon = \varepsilon_1$ $W_1 = ?$

$$\varepsilon = 0 \quad W_0 = 1$$

a) What is the probability that a given molecule is in each state, p_0 and p_1 , as a function of W_1 , ε_1 , and T .

$$p_0 = \frac{1}{1 + W_1 e^{-\varepsilon_1/kT}} \quad p_1 = \frac{W_1 e^{-\varepsilon_1/kT}}{1 + W_1 e^{-\varepsilon_1/kT}}$$

b) What is the total (*not* single particle) partition function for this system?

$$Q = [1 + W_1 e^{-\varepsilon_1/kT}]^N$$

c) Find the energy of this system, U , directly from the partition function.

$$q = 1 + W_1 e^{-\beta\varepsilon_1} \quad U = -N \frac{\partial \ln q}{\partial \beta} = \frac{W_1 N \varepsilon_1 e^{-\beta\varepsilon_1}}{1 + W_1 e^{-\beta\varepsilon_1}}$$

d) Find the energy of this system, U , directly from your probabilities in (a).

$$U = Np_0 \cdot 0 + Np_1 \varepsilon_1 = \frac{W_1 N \varepsilon_1 e^{-\beta\varepsilon_1}}{1 + W_1 e^{-\beta\varepsilon_1}}$$

e) Measurements of the specific heat of one mole ($N=N_A=6.022 \times 10^{23}$) of this system find the following behavior for the energy U as a function of T . Sketch the C_V that was measured, at right. Don't worry about the scale, but accurately sketch and label the shape of the curve.

f) What is the (constant) asymptotic energy of this system in the high temperature limit?

$$T \rightarrow \infty \Rightarrow \beta = \frac{1}{kT} \rightarrow 0 \Rightarrow U \rightarrow \frac{NW_1 \varepsilon_1}{1 + W_1}$$

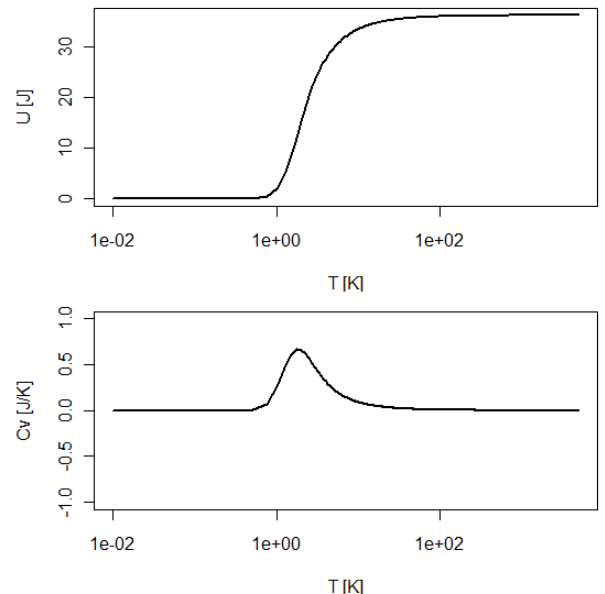
g) If the energy at low temperatures is measured to be approximately $U \approx Ae^{-B/T}$, where $A = 291.07$ J and $B = 5.00$ K, find W_1 , and ε_1 .

$$T \rightarrow 0 \Rightarrow \beta = \frac{1}{kT} \rightarrow \infty \Rightarrow U \rightarrow NW_1 \varepsilon_1 e^{-\varepsilon_1/kT}$$

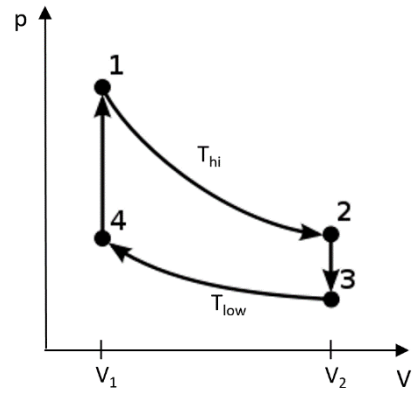
$$\Rightarrow A = NW_1 \varepsilon_1, \quad B = \varepsilon_1 / k$$

$$\varepsilon_1 = Bk = 6.905 \text{e-} 23 \text{ J}$$

$$W_1 = A / N_A \varepsilon_1 = 291.07 / (6.022 \times 10^{23} \times 6.905 \text{e-} 23) = 7$$



5. The Stirling cycle consists of an isothermal expansion (1→2) at $T=T_{hi}$, a constant Volume cooling (2→3) at V_2 , an isothermal compression (3→4) at $T=T_{low}$, and a constant Volume compression (4→1) at V_1 . In all parts below, assume that $T_{hi} > T_{low}$, $V_2 > V_1$, assume that the system consists of a diatomic ideal gas with a constant volume specific heat C_V which can be assumed a constant, and assume $N=\text{const}$ and $dN=0$.



a) Find the work done on the system in each phase of the cycle W_{12} , W_{23} , W_{34} , W_{41} , and the total work done by the system W_{by} .

$$W_{12} = -\int_{V_1}^{V_2} \frac{NkT_{hi}}{V} dV = NkT_{hi} \ln \frac{V_1}{V_2} \quad W_{23} = 0 \quad W_{34} = -\int_{V_3}^{V_4} \frac{NkT_{lo}}{V} dV = NkT_{lo} \ln \frac{V_2}{V_1} \quad W_{41} = 0$$

b) Find the energy change of the system in each phase of the cycle ΔU_{12} , ΔU_{23} , ΔU_{34} , and ΔU_{41} in terms of C_V .

$$\Delta U_{12} = 0 \quad \Delta U_{23} = C_V(T_{lo} - T_{hi}) \quad \Delta U_{34} = 0 \quad \Delta U_{41} = C_V(T_{hi} - T_{lo})$$

c) Find the heat added to the system in each phase of the cycle Q_{12} , Q_{23} , Q_{34} , Q_{41} .

$$Q_{12} = \Delta U_{12} - W_{12} = NkT_{hi} \ln \frac{V_2}{V_1} \quad Q_{23} = \Delta U_{23} - W_{23} = C_V(T_{lo} - T_{hi})$$

$$Q_{34} = \Delta U_{34} - W_{34} = NkT_{lo} \ln \frac{V_1}{V_2} \quad Q_{41} = \Delta U_{41} - W_{41} = C_V(T_{hi} - T_{lo})$$

d) Find the enthalpy change ΔH_{12}

$$\Delta H_{12} = \Delta U_{12} + p_2V_2 - p_1V_1 = Nk(T_2 - T_1) = 0$$

e) Find the efficiency of the Stirling cycle, η , considering the output work W_{by} and the input heat that must be added to the system. Only the heat added to the system needs to be considered input energy; if heat leaves the system in during a phase of the cycle, that heat can be ignored when calculating the efficiency.

$$\eta = \frac{W_{by}}{Q_{12} + Q_{41}} = \frac{-W_{12} - W_{34}}{NkT_{hi} \ln \frac{V_2}{V_1} + C_V(T_{hi} - T_{lo})} = \frac{Nk(T_{hi} - T_{lo}) \ln \frac{V_2}{V_1}}{NkT_{hi} \ln \frac{V_2}{V_1} + C_V(T_{hi} - T_{lo})} = \frac{T_{hi} - T_{lo}}{T_{hi} + C_V(T_{hi} - T_{lo}) / Nk \ln \frac{V_2}{V_1}}$$

f) Find a simple expression for the entropy change in the isothermal processes:

$\Delta S_{12} = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V} \right)_{T,N} dV$ and $\Delta S_{34} = \int_{V_2}^{V_1} \left(\frac{\partial S}{\partial V} \right)_{T,N} dV$ using $\left(\frac{\partial S}{\partial V} \right)_{T,N} = \left(\frac{\partial S}{\partial V} \right)_{U,N} = \frac{p}{T} = \frac{Nk}{V}$ for an ideal gas.

$$\Delta S_{12} = \int_{V_1}^{V_2} \frac{Nk}{V} dV = Nk \ln \frac{V_2}{V_1} \quad \Delta S_{34} = \int_{V_2}^{V_1} \frac{Nk}{V} dV = Nk \ln \frac{V_1}{V_2}$$

g) Find a simple expression for the entropy change in the constant volume processes:

$$\Delta S_{41} = \int_{T_{low}}^{T_{hi}} \left(\frac{\partial S}{\partial T} \right)_{V,N} dT \quad \text{and} \quad \Delta S_{23} = \int_{T_{hi}}^{T_{low}} \left(\frac{\partial S}{\partial T} \right)_{V,N} dT \quad \text{using} \quad \left(\frac{\partial S}{\partial T} \right)_{V,N} = \left(\frac{\partial S}{\partial U} \right)_{V,N} \left(\frac{\partial U}{\partial T} \right)_{V,N}$$

$$\left(\frac{\partial S}{\partial T}\right)_{V,N} = C_V/T$$

$$\Delta S_{41} = \int_{T_{lo}}^{T_{hi}} \frac{C_V}{T} dT = C_V \ln \frac{T_{hi}}{T_{lo}} \quad \Delta S_{23} = \int_{T_{hi}}^{T_{lo}} \frac{C_V}{T} dT = C_V \ln \frac{T_{lo}}{T_{hi}}$$

h) What is the total entropy change of the system in one full cycle: ΔS_{12341} ?
zero

6. a) If $C_V = \alpha Nk$, where $\alpha > 0$ is a constant, for a system of N indistinguishable particles, how does the single particle partition function, q , depend on T , i.e. what is $q(T)$? Don't worry about constants of integration.

$$C_V = \alpha Nk = \left(\frac{\partial U}{\partial T}\right)_{V,N} \rightarrow U = \alpha NkT = kT^2 \left(\frac{\partial}{\partial T} \ln \frac{q^N}{N!}\right)_{V,N} \rightarrow \left(\frac{\partial}{\partial T} \ln \frac{eq}{N}\right)_{V,N} = \frac{\alpha}{T}$$

$$\rightarrow \ln \frac{eq}{N} = \alpha \ln T \rightarrow q = q_0 T^\alpha$$

b) Recall that the Sackur-Tetrode entropy $S = Nk \ln \frac{cT^{3/2}V}{N}$ applies to a monatomic ideal gas.

For a diatomic ideal gas with translational and rotational states excited, this expression changes to

$S = Nk \ln \frac{cT^{5/2}V}{N}$. Use this expression to find a simple expression for the entropy changes in each phase in the Stirling cycle of problem 5: ΔS_{12} , ΔS_{23} , ΔS_{34} , and ΔS_{41} .

$$\Delta S_{12} = Nk \ln \frac{cT_2^{5/2}V_2}{N} - Nk \ln \frac{cT_1^{5/2}V_1}{N} = Nk \ln \frac{V_2}{V_1}$$

$$\Delta S_{23} = Nk \ln \frac{cT_3^{5/2}V_3}{N} - Nk \ln \frac{cT_2^{5/2}V_2}{N} = \frac{5}{2} Nk \ln \frac{T_{lo}}{T_{hi}}$$

$$\Delta S_{34} = Nk \ln \frac{cT_4^{5/2}V_4}{N} - Nk \ln \frac{cT_3^{5/2}V_3}{N} = Nk \ln \frac{V_1}{V_2}$$

$$\Delta S_{41} = Nk \ln \frac{cT_1^{5/2}V_1}{N} - Nk \ln \frac{cT_4^{5/2}V_4}{N} = \frac{5}{2} Nk \ln \frac{T_{hi}}{T_{lo}}$$

c) Which of your expressions in 3c) are consistent with what you found in 4f) and 4g)? Why?

All because $C_V = \frac{5}{2} Nk$

7. Consider three compression processes of an initial volume of 1 m^3 of an ideal gas, originally at $p_A = 10^5 \text{ N/m}^2$, to a final volume of 0.2 m^3 , as shown below. $A \rightarrow B$ is isobaric (constant pressure), $A \rightarrow C$ is isothermal, and $A \rightarrow D$ is adiabatic.

a) Calculate the work done **on** the system, in J, in the isobaric compression, $A \rightarrow B$.

$$W_{AB} = -\int p, dV = -p(V_B - V_A) = -1e5(-.8) = 80 \text{ kJ}$$

b) Calculate the work done on the system, in J, in the isothermal compression, $A \rightarrow C$.

$$W_{AC} = -\int p, dV = -\int (NkT/V, dV) = -[NkT \ln V] = -p_A V_A [\ln V_B / V_A] = -1 \ln(.2) = 160.9 \text{ kJ}$$

c) Calculate the work done on the system, in J, in the adiabatic compression, $A \rightarrow D$. Recall that for an adiabatic expansion of an ideal gas, $pV^\gamma = \text{const}$, where $\gamma = C_p / C_v$. For this gas $\gamma = 7/5$.

$$W_{AD} = -\int p, dV = -\int (c/V^{1.4}, dV) = 2.5c[1/V_B^{.4} - 1/V_A^{.4}] = 2.5p_A V_A^{1.4}[1/V_B^{.4} - 1/V_A^{.4}] = 225.9 \text{ kJ}$$

For (d) through (j) below, you may use $U = C_v T$ and $C_v = \frac{5}{2} Nk$ is constant for this gas.

d) How much heat, in J, is removed from the system during the isothermal compression $A \rightarrow C$ to hold the temperature constant?

$$U = \text{const.} \quad dU = dQ + dW \quad dQ = dU - dW = -dW = -160.9 \text{ kJ (removed)}$$

e) How much heat, in J, is removed from the system during the isobaric process to hold the pressure constant during the isobaric compression $A \rightarrow B$?

$$NkT = pV \rightarrow dU = d(C_v T) = d(2.5NkT) = d(2.5pV) = 2.5(p_B V_B - p_A V_A) = 2.5(.2e5 - 1e5) = -200 \text{ kJ}$$

$$(200 \text{ kJ removed})$$

$$dQ = dU - dW = -200 \text{ kJ} - 80 \text{ kJ} = -280 \text{ kJ} \quad (\text{removed})$$

f) How much heat, in J, is removed from the system during the adiabatic process $A \rightarrow D$?

$$dQ = 0$$

g) If $\gamma = C_p / C_v = 7/5$, do you think the gas is monatomic or diatomic? Why? Recall that $C_p = C_v + Nk$ for an ideal gas.

Diatomic so that $C_v = (5/2)Nk$ and $C_p = (7/2)Nk$

For h)-j) assume the system is one mole of gas, so $R = Nk = 8.314 \text{ J/K}$ and $T = 300 \text{ K}$.

h) What is the change in energy of the system in the isothermal compression from $A \rightarrow C$,

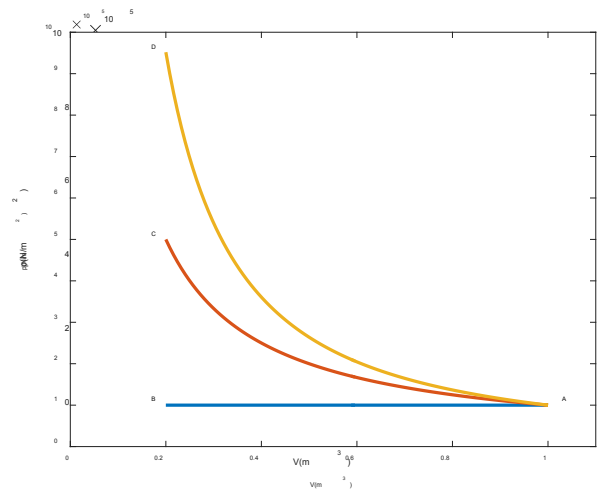
$$\Delta U = U_C - U_A?$$

zero

i) What is the change in enthalpy of the system in the isothermal compression from $A \rightarrow C$,

$$\Delta H = H_C - H_A?$$

$$dH = dU + d(pV) = \text{zero} + (p_C V_C - p_A V_A) = (5 \cdot .2 - 1) = 0$$



j) What is the change in the entropy of the system in the isothermal compression from A→C
 $\Delta S = S_C - S_A$?
 $dS = dQ/T = -160.9 \text{ kJ}/300 \text{ K} = -536.5 \text{ J/K}$

8. Consider a system of N distinguishable particles with equally spaced energy levels $\varepsilon_l = (l-1)\varepsilon_0$, $l \in [1, 2, \dots, \infty)$, and multiplicity $W_l = l$, i.e. higher energy levels have more microstates. The system is in equilibrium with a reservoir at fixed temperature, T .

a) Write an expression for the single particle partition function, q , of this system (you do not need to evaluate the sum, but include limits on l).

b) Write an expression for the total partition function, Q , of this system, in terms of q in a).

c) Write an expression for the energy per particle, $\langle \varepsilon \rangle$, of this system (you do not need to evaluate the sum, but include limits on l). You may use your q from (a).

a) Write an expression for the single particle partition function, q , of this system (you do not need to evaluate the sum, but include limits on l).

$$q = \sum_{l=1}^{\infty} l e^{-\frac{(l-1)\varepsilon_0}{kT}}$$

b) Write an expression for the total partition function, Q , of this system, in terms of q in a).

$$Q = q^N$$

c) Write an expression for the energy per particle, $\langle \varepsilon \rangle$, of this system (you do not need to evaluate the sum, but include limits on l). You may use your q from (a).

$$\langle \varepsilon \rangle = \frac{\sum_{l=1}^{\infty} l(l-1)\varepsilon_0 e^{-\frac{(l-1)\varepsilon_0}{kT}}}{\sum_{l=1}^{\infty} l e^{-\frac{(l-1)\varepsilon_0}{kT}}}$$

9. Fish kills. Extended periods of high temperatures (or global warming) can reduce the oxygen dissolved in lakes and oceans and cause fish populations to suffocate. You are going to calculate the magnitude of this effect. Consider O_2 dissolved in water and in equilibrium with its vapor.

a) At equilibrium, what constraint involving the chemical potentials of either the liquid or vapor O_2 , or the liquid water, is satisfied?

$$\mu_{\text{O}_2}^{\text{vapor}} = \mu_{\text{O}_2}^{\text{liquid}}$$

b) How is the chemical potential of O_2 in the vapor phase related to its single particle partition function, q ?

$$\mu_{O_2}^{vapor} = -kT \ln \frac{q}{N}$$

c) We are interested in the temperature and pressure dependence of the chemical potentials, so write the single particle partition function for vapor O₂ in the form $q = cV^a T^b$, where a , b , and c are constants. The constants $a = 1$ and $b = 5/2$ for O₂ when translational and rotational states are excited but vibrational states are not. Using these constants, rewrite the chemical potential for

vapor O₂ as a function of only c , k , p , and T . We have often used the expression $\mu = kT \ln \frac{P}{P_{int}^0}$

for an ideal gas, but for this problem we need to know how $P_{int}^0 = \frac{qkT}{V}$ depends on T . If you

can't get the full expression for $\mu_{O_2}^{vapor}$, use $\mu = kT \ln \frac{P}{P_{int}^0}$ for the remaining parts of this problem.

Translation $q \sim VT^{3/2}$ Rotation (diatom) $q \sim T$ $q = cVT^{5/2}$ $a = 1, b = 5/2$

$$\frac{q}{N} = \frac{cVT^{5/2}}{N} = \frac{ckT^{7/2}}{p}$$

$$\mu_{O_2}^{vapor} = -kT \ln \frac{ckT^{7/2}}{p}$$

d) For the liquid phase O₂ we will use the regular solution model. Write down or derive an expression for the chemical potential of O₂ in the liquid phase. You may assume that x_{O_2} , the dissolved O₂ concentration, is dilute, i.e. $x_{O_2} \ll 1$. Simplify this expression so that it depends on the coordination number z , w_{wO} , w_{OO} , and w_{ww} instead of χ_{AB} , where w_{wO} , w_{OO} , and w_{ww} are the energies of interaction between water and O₂, O₂ and O₂, and water-water, respectively. You may

use $\Delta h_{solution}^0 = z \left(w_{wO} - \frac{w_{ww}}{2} \right)$ to simplify your expression.

$$\frac{\mu_{O_2}^{vapor}}{kT} = \ln x_{O_2} + \frac{zw_{OO}}{2kT} + \chi_{AB} (1 - x_{O_2}^2) \approx \ln x_{O_2} + \frac{zw_{OO}}{2kT} + \chi_{AB}$$

$$\chi_{AB} = \frac{z}{kT} \left(w_{OO} - \frac{w_{wO} + w_{ww}}{2} \right)$$

$$\mu_{O_2}^{vapor} = kT \ln x_{O_2} + zw_{wO} - \frac{zw_{ww}}{2}$$

$$\mu_{O_2}^{vapor} = kT \ln x_{O_2} + \Delta h_{soln}^0$$

e) Now use part a) c) and d) to relate the vapor pressure of O₂ to the temperature and concentration of dissolved O₂, x_{O_2} . You can keep x_{O_2} in terms of the particle fractions.

$$\mu_{O_2}^{vapor} = kT \ln x_{O_2} + \Delta h_{soln}^0 = -kT \ln \frac{ckT^{7/2}}{p}$$

$$p_{O_2} = x_{O_2} ckT^{7/2} e^{\Delta h_{soln}^0 / kT}$$

f) For most gases, the enthalpy change of dissolution, $\Delta h_{\text{solution}}^0 < 0$, so going into solution is exothermic. If the enthalpy change of dissolution of O_2 in water is

$$\Delta h_{\text{solution}}^0 = z \left(w_{wO} - \frac{w_{ww}}{2} \right) = -2.4 \times 10^{-20} \text{ J/molecule, calculate the concentration of } O_2 \text{ dissolved in}$$

water at $T=300\text{K}$, if air is 21% O_2 so that the vapor pressure of O_2 is $21,300 \text{ N/m}^2$. The Henry's law constant for O_2 at $T=300\text{K}$ is $k_h = p_{\text{int}}^0 \exp(\Delta h_{\text{solution}}^0 / kT) = 4.4 \times 10^9 \text{ N/m}^2$. Remember that p_{int}^0 , defined in d) also depends on T , so the Henry's law constant is not really a constant.

$$p_{\text{int}}^0 = \frac{qkT}{V} = ckT^{7/2}$$

$$p_{O_2} = p_{\text{int}}^0 e^{\Delta h_{\text{soln}}^0 / kT} = k_H x_{O_2}$$

$$x_{O_2} = \frac{21,300 \text{ N/m}^2}{4.4 \times 10^9 \text{ N/m}^2} = 4.84 \times 10^{-6}$$

g) Now find the concentration of O_2 dissolved in water at $T=305\text{K}$. By what fraction is the

oxygen concentration reduced, $f = \frac{x_{O_2}^{305\text{K}}}{x_{O_2}^{300\text{K}}}$?

$$x_{O_2}^{305} = \frac{p_{O_2}}{ckT^{7/2} e^{\Delta h_{\text{soln}}^0 / kT}} \quad \text{and} \quad x_{O_2}^{300} = \frac{p_{O_2}}{ckT_0^{7/2} e^{\Delta h_{\text{soln}}^0 / kT_0}} \quad \text{where the pressures are the same and}$$

$T_0=300\text{K}$ and $T=305\text{K}$, so eliminating p_{O_2} :

$$x_{O_2}^{305} = \frac{p_{O_2}}{ckT^{7/2} e^{\Delta h_{\text{soln}}^0 / kT}} = \frac{x_{O_2}^{300} ckT_0^{7/2} e^{\Delta h_{\text{soln}}^0 / kT_0}}{ckT^{7/2} e^{\Delta h_{\text{soln}}^0 / kT}} = x_{O_2}^{300} \left(\frac{T_0}{T} \right)^{7/2} e^{\Delta h_{\text{soln}}^0 (1/kT_0 - 1/kT)}$$

$$\frac{x_{O_2}^{305}}{x_{O_2}^{300}} = \left(\frac{300}{305} \right)^{7/2} e^{\frac{-2.4 \times 10^{-20}}{1.38 \times 10^{-23}} \left(\frac{1}{300} - \frac{1}{305} \right)} = (.944)(.909) = (.858)$$

$$f = 0.858$$

h) Assuming an isothermal atmosphere at $T=300\text{K}$, at what altitude is the oxygen concentration reduced by this same fraction (f from (h) above) from sea level O_2

pressure? The mass of an Oxygen atom is $m_{O_2} = 32m_p$ and the mass of the proton is

$$m_p = 1.67 \times 10^{-27} \text{ kg.}$$

$$p = p_0 \exp(-mgh/kT)$$

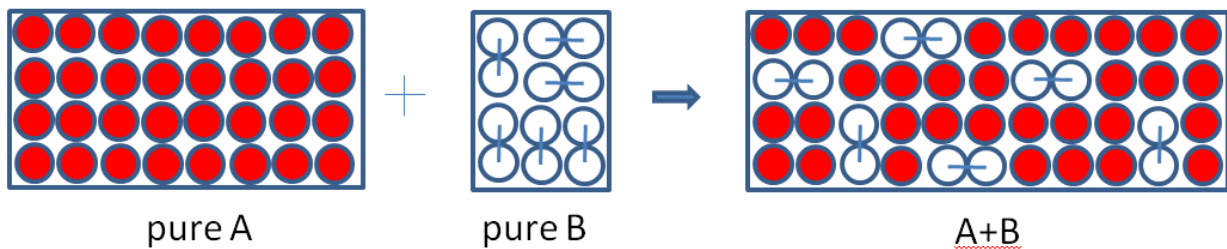
$$p_1/p_0 = \exp(-mgh/kT) = .858$$

$$h = (kT/mg)(-\log(.858)) = (1.38 \times 10^{-23} \times 300) / (1.67 \times 10^{-27} \times 32 \times 9.81) \times (.0665) = 1.21 \text{ km}$$

i) In physical terms, why does increased temperature cause less dissolved O_2 ? Consider both the entropy of mixing and the entropy of the gas molecules.

Going into liquid is both entropically and energetically favored $\Delta s_{\text{solution}}^0 = -k \ln x_{O_2} > 0$ and $\Delta h_{\text{solution}}^0 < 0$, but going into vapor is also entropically favored $\Delta s_{\text{solution}}^0 = k \ln \frac{ckT^{7/2}}{p} > 0$ until the pressure gets high enough. At equil $\Delta h_{\text{solution}}^0 = \frac{\Delta s_{\text{solution}}^0 + \Delta s_{\text{vapor}}^0}{T}$. Since pressure is fixed here, raising T means lower concentrations are required to balance $\Delta h_{\text{solution}}^0$.

10. Consider a lattice model of mixing monomeric molecules (A), occupying single lattice sites, and linear dimeric molecules (B), occupying two adjacent lattice sites, in M total lattice sites with coordination number z . The dimeric and monomeric molecules don't react—i.e., the number of dimers and monomers is fixed, the dimeric bonds cannot be broken or formed.



Use Stirling's approximation throughout. You may use the fact that the multiplicity of mixing n_p polymer molecules of length L in n_s molecules solvent is:

$$W(n_s, n_p, L) = \left(\frac{z}{M}\right)^{n_p} \left(\frac{z-1}{M}\right)^{(L-2)n_p} \frac{M!}{(M - Ln_p)! n_p!}$$

a) What is the entropy of the pure A (monomer) state?

$$S_{\text{monomer}} = 0$$

b) What is the entropy of the pure B (dimer) state? (Eliminate M).

$$n_p = n_d \text{ (number of dimers)}$$

$$M = n_s + Ln_p = 2n_p. \text{ For } L = 2, W_d = \left(\frac{z}{2n_d}\right)^{n_d} \frac{(2n_d)!}{n_d!} \approx \left(\frac{z}{2n_d}\right)^{n_d} \frac{\left(\frac{2n_d}{e}\right)^{2n_d}}{\left(\frac{n_d}{e}\right)^{n_d}} \approx \left(\frac{2z}{e}\right)^{n_d}$$

$$S_d = k \ln W_d = n_d k \ln \left(\frac{2z}{e}\right) \quad \text{(Each of the } n_d \text{ bonds can be in approx } z \text{ states, reduced by packing constraints.)}$$

c) If a) and b) are different, why?

Dimers have orientation entropy. Monomers have only one distinguishable configuration, dimers have many distinguishable configurations.

d) What is the entropy of the mixed state? $n_p = n_d \quad n_s = n_m$

$$\text{Now } W = \left(\frac{z}{M}\right)^{n_d} \frac{(M)!}{n_s! n_p!} \approx \left(\frac{z}{M}\right)^{n_d} \frac{\left(\frac{M}{e}\right)^M}{\left(\frac{n_s}{e}\right)^{n_s} \left(\frac{n_d}{e}\right)^{n_d}} \approx \left(\frac{z}{M}\right)^{n_d} \frac{\left(\frac{M}{e}\right)^{n_s} \left(\frac{M}{e}\right)^{2n_d}}{\left(\frac{n_s}{e}\right)^{n_s} \left(\frac{n_d}{e}\right)^{n_d}} = \left(\frac{z}{e}\right)^{n_d} \left(\frac{M}{n_s}\right)^{n_s} \left(\frac{M}{n_d}\right)^{n_d}$$

$$S = k \ln W = k[n_d \ln(z/e) + n_m \ln(M/n_m) + n_d \ln(M/n_d)]$$

e) What is the entropy of mixing, $\frac{\Delta S_{mix}}{Mk}$, in terms of the volume fraction of dimers, $\phi_d = 2n_d / M$, and the volume fraction of monomers, $\phi_m = n_m / M$?

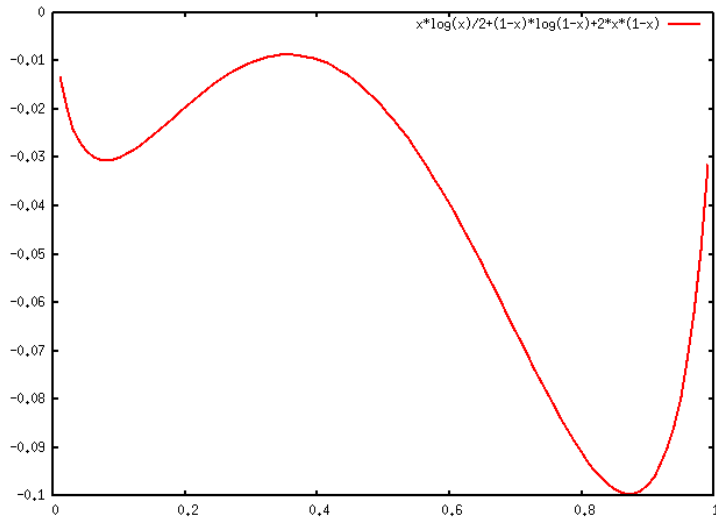
$$\Delta S_{mix} = S - S_d = k[n_d \ln(z/e) + n_m \ln(M/n_m) + n_d \ln(M/n_d)] - kn_d \ln(2z/e)$$

$$\Delta S_{mix} = k[-n_d \ln(2) - n_m \ln(n_m/M) - n_d \ln(n_d/M)] = k[-n_m \ln(n_m/M) - n_d \ln(2n_d/M)]$$

$$\frac{\Delta S_{mix}}{Mk} = -\phi_m \ln \phi_m - \frac{\phi_d}{2} \ln \phi_d$$

11. Assume that the total free energy change of mixing for the dimeric/monomeric mixing model of problem 10 is: $\frac{\Delta F_{mix}}{MkT} = \frac{1}{L} x \ln x + (1-x) \ln(1-x) + \chi x(1-x)$, where $x = \phi_d = 2n_d / M$ is the volume fraction of dimeric molecules, M is the total number of lattice sites, and χ is the exchange parameter, and $L=2$ is the length of the dimer. A plot of

$\frac{\Delta F_{mix}}{MkT} = \frac{1}{2} x \ln x + (1-x) \ln(1-x) + 2x(1-x)$ is shown below, for $L=2$ and $\chi=2$.



a) If the imposed volume fraction of dimeric molecules is $x_0=0.4$ for the case $L=2$ and $\chi=2$, does uniform mixing of dimers and monomers occur, or will the solution separate into two phases? Why?

Separate. $\Delta F_{mix}(x_0) > \text{common tangent line}$.

b) If the imposed volume fraction of dimers is $x_0=0.05$ for the case $L=2$ and $\chi=2$, does uniform mixing of dimers and monomers occur, or will the solution separate into two phases? Why?

One uniform phase. $x_0 < x'$.

c) If phase separation happens, find a constraint which uniquely specifies the volume fractions of dimer in the two phases at equilibrium: x' , the more monomer rich phase, and x'' , the more dimer rich phase, for $L=2$ and $\chi=2$. This constraint determines the volume fraction of dimer, x' and x'' , of the two phases at equilibrium. You don't have to solve for x' and x'' .

Let $F = \frac{\Delta F_{mix}}{MkT}$.

Common tangent condition: (A) $\left. \frac{\partial F}{\partial x} \right|_{x'} = \left. \frac{\partial F}{\partial x} \right|_{x''}$ and (B) $F(x') - x' \left. \frac{\partial F}{\partial x} \right|_{x'} = F(x'') - x'' \left. \frac{\partial F}{\partial x} \right|_{x''}$.

(B) can also be written: $F(x'') = F(x') + \left. \frac{\partial F}{\partial x} \right|_{x' \text{ or } x''} (x'' - x')$

$$F(x) = \frac{1}{2} x \ln x + (1-x) \ln(1-x) + 2x(1-x)$$

$$\frac{\partial F}{\partial x} = \frac{1}{2} (1 + \ln x) - \ln(1-x) - 1 + 2 - 4x = \frac{1}{2} \ln x - \ln(1-x) + \frac{3}{2} - 4x$$

d) Demonstrate whether or not $x'=0.059567$ and $x''=0.84906$ satisfy your constraint in c). Does $x'=0.059567$ and $x''=0.43676$ satisfy your constraint in c)?

x	$\frac{\partial F}{\partial x}$	$F(x) - x \frac{\partial F}{\partial x}$
$x' = 0.059567$	-.08718	-.02453
$x = 0.43676$	-.08718	.02585
$x'' = 0.84906$	-.08718	-.02454

$x' = 0.059567$ and $x'' = 0.84906$ satisfy both (A) and (B)

$x' = 0.059567$ and $x = 0.43676$ satisfy only (A)

e) Using the first set of values for x' and x'' from d), find the volume fraction, f , of the total mixture that will be in the monomer rich phase in equilibrium if $x_0=0.4$, $L=2$, and $\chi=2$. What volume fraction of the total mixture will be in the dimer rich phase?

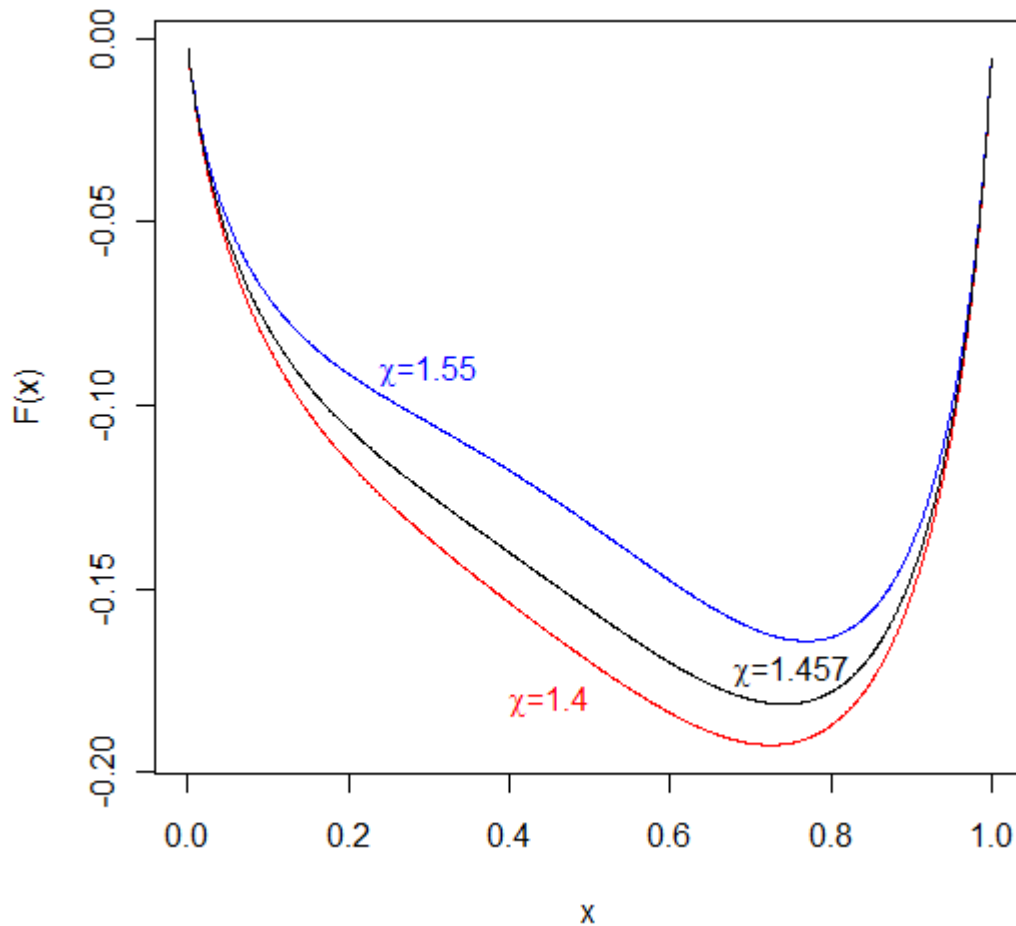
$$f = \frac{x_0 - x'}{x'' - x'} = \frac{0.4 - 0.059567}{0.84906 - 0.059567} = .4312 \text{ at } x'' = 0.84906 \text{ (dimer rich)}$$

$$1 - f = .5688 \text{ at } x' = 0.059567$$

f) On thermodynamic grounds, why do the phases separate, since $\frac{\Delta F_{mix}}{MkT} < 0$ for $x_0=0.4$?

Uniform phase has $\Delta F_{mix}(x_0) < 0$, but a state separated into two mixed phases at x' and x'' has even lower ΔF .

g) What is the critical value of χ for $L=2$, below which phase separation never occurs for any concentration?



Phase separation does not occur unless there is a central region of negative curvature of $F(x)$.

$$\frac{\partial^2 F}{\partial x^2} = \frac{1}{2x} + \frac{1}{1-x} - 2\chi. \quad \frac{\partial^2 F}{\partial x^2} = 0 \text{ has two roots which come together at } \chi_{crit}.$$

$$\frac{\partial^2 F}{\partial x^2} = 0 \rightarrow x^2 + \left(1 - \frac{1}{4\chi}\right)x + \frac{1}{4\chi} = 0. \quad \text{Roots coalesce when } b^2 - 4ac = 0 \text{ or}$$

$$\chi = \frac{1}{4(3 - 2\sqrt{2})} = 1.457$$

Can also use the fact that roots of $\frac{\partial^2 F}{\partial x^2} = 0$ coalesce when $\frac{\partial^3 F}{\partial x^3} = \frac{-1}{2x^2} + \frac{1}{(1-x)^2} = 0$ which happens at $x = -1 + \sqrt{2} = 0.4142$, and using this x in $\frac{\partial^2 F}{\partial x^2} = 0$ gives $\frac{1}{2(\sqrt{2}-1)} + \frac{1}{2-\sqrt{2}} = 2\chi$ or $\chi = \frac{1}{4(3-2\sqrt{2})} = 1.457$.

h) What values of x' and x'' are on the spinodal curve for metastability for $L=2$ and $\chi=2$?

$$x^2 + \left(1 - \frac{1}{4\chi}\right)x + \frac{1}{4\chi} = 0 \rightarrow x^2 + \frac{7}{8}x + \frac{1}{8} = 0 \rightarrow x = \frac{7}{16} \pm \frac{\sqrt{17}}{16}. \quad x' = .1798 \text{ and } x'' = .6952.$$

i) How are the chemical potentials of dimers and monomers in the two phases

($\mu'_{\text{dimer}}, \mu''_{\text{dimer}}, \mu'_{\text{monomer}}, \mu''_{\text{monomer}}$) related?

$$\mu'_{\text{dimer}} = \mu''_{\text{dimer}} \quad \text{and} \quad \mu'_{\text{monomer}} = \mu''_{\text{monomer}}$$

12. Derive the Gibbs-Helmoltz relation $\left(\frac{\partial(G/T)}{\partial T}\right)_{p,N} = -\frac{H}{T^2}$.

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{T\left(\frac{\partial G}{\partial T}\right)_p - G}{T^2}$$

$$G = H - TS \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{-TS - (H - TS)}{T^2} = -\frac{H}{T^2}$$

13. Calculate the spinodal (metastability) curve and the critical point for the lattice model of mixing. If $\chi=3$, what are the concentration ranges for global stability and metastability? If the imposed fraction of A is $x_0=0.3$, what is the concentration and mole fraction of the A rich phase and the B rich phase in equilibrium?

$$\text{Lattice model of mixing: } \frac{\Delta F_{\text{mix}}}{NkT} = \chi_{AB}x(1-x) + x \ln x + (1-x) \ln(1-x)$$

$$\text{spinodal curve: } \frac{\partial^2 F}{\partial x^2} = 0 \quad \frac{\partial F}{\partial x} = \chi_{AB}(1-2x) + \ln x - \ln(1-x)$$

$$\frac{\partial^2 F}{\partial x^2} = -2\chi_{AB} + \frac{1}{x} + \frac{1}{1-x} = 0$$

$$\frac{1}{\chi_{AB}} = 2x(1-x) \quad (\text{plotted in Fig 25.12})$$

For $\chi_{AB} = 3$, metastable curve: $\frac{1}{6} = x(1-x)$, $x = \frac{1}{2} \left(1 \pm \frac{\sqrt{3}}{3} \right)$, $x' = .211, x'' = .789$

For $\chi_{AB} = 3$, binodal (global stability) curve from common tangent condition, in this simple symmetric case: $\frac{\partial F}{\partial x} = \chi_{AB}(1-2x) + \ln x - \ln(1-x) = 0$

$6(x - \frac{1}{2}) = \ln \frac{x}{1-x}$. Solve numerically: $x' = .0707, x'' = .9293$. (Soln at $x=0.5$ doesn't satisfy common tangent cond.) (You won't have to solve eqns like this numerically on the exam, but you should understand the solutions.)

So for $\chi_{AB} = 3$: If $x_0 = (0, 0.0707)$: one mixed phase is stable. If $x_0 = (0.0707, .211)$, system is in metastable range, and will separate if perturbed (eventually) into two phases of concentration .0707 and .9293. If $x_0 = (.211, .789)$, system is unstable and will immediately separate into two phases of concentration .0707 and .9293. If $x_0 = (0.789, .9293)$, system is in metastable range, and will separate if perturbed (eventually) into two phases of concentration .0707 and .9293. If $x_0 = (.9293, 1)$: one mixed phase is stable.

If $x_0 = 0.3$, by lever rule $f = (.3 - .0707) / (.9293 - .0707) = .267$ of system will be in phase at concentration .9293, $1-f = .733$ of system will be in phase at concentration .0707.

14. The potassium ion concentration inside a nerve cell at 25°C is found to be 20 times higher than the concentration outside the cell. In contrast, the sodium ion concentration is 20 times higher outside the cell than inside. The potential difference across the cell membrane is 77 mV, with the inside negative relative to the outside. Identify which component is transported actively (pumped across the membrane), and which component is freely permeable to the membrane.

Calculating the electrochemical potentials, $\mu' = \mu^0 + kT \ln c + ze\psi$, for both ion species:

$$\mu'_{in} = \mu^0_{in} + kT \ln c_{in} + ze\psi_{in} \quad \mu'_{out} = \mu^0_{out} + kT \ln c_{out} + ze\psi_{out}$$

$$\mu'_{in} - \mu'_{out} = kT \ln c_{in} - kT \ln c_{out} + ze(\psi_{in} - \psi_{out}) = kT \ln \frac{c_{in}}{c_{out}} + ze(\psi_{in} - \psi_{out})$$

For $\text{Na}^+ (z=1)$:

$$\mu'_{in} - \mu'_{out} = kT \ln \frac{c_{in}}{c_{out}} + e(\psi_{in} - \psi_{out}) = 1.38 \times 10^{-23} (298) \ln(.05) + 1.6 \times 10^{-19} (-0.077) = -2.5 \times 10^{-20}$$

For $\text{K}^+ (z=1)$:

$$\mu'_{in} - \mu'_{out} = kT \ln \frac{c_{in}}{c_{out}} + e(\psi_{in} - \psi_{out}) = 1.38 \times 10^{-23} (298) \ln(20) - 1.6 \times 10^{-19} (0.077) = -3.5 \times 10^{-25}$$

(≈ 0 within the precision of the voltage measurement)

So Na^+ is actively transported (sodium pump) and K^+ is in equilibrium.

15. Consider a lattice model of a solution of small solvent molecules of three types, A, B, and C, of equal size, filling a total of $M = N_A + N_B + N_C$ lattice sites. Each lattice site has z nearest neighbors. Consider the mixing of pure A, B, and C to produce a uniform phase of A+B+C.

a) Starting from the definition of entropy, calculate the entropy of mixing, $\Delta S_{mix}(x_A, x_B, x_C)$, where $x_A = N_A/M$, $x_B = N_B/M$, $x_C = N_C/M$, assuming $N_A, N_B, N_C \gg 1$.

$$S(pure_A + pure_B + pure_C) = 0$$

$$\Delta S_{mix}(x_A, x_B, x_C) = S(x_A, x_B, x_C) = k \ln \frac{M!}{N_A! N_B! N_C!}$$

$$\frac{\Delta S_{mix}(x_A, x_B, x_C)}{k} = M \ln M - M - N_A \ln N_A + N_A - N_B \ln N_B + N_B - N_C \ln N_C + N_C$$

$$\frac{\Delta S_{mix}(x_A, x_B, x_C)}{k} = (N_A + N_B + N_C) \ln M - N_A \ln N_A - N_B \ln N_B - N_C \ln N_C$$

$$\Delta S_{mix}(x_A, x_B, x_C) = -Mk [x_A \ln x_A + x_B \ln x_B + x_C \ln x_C]$$

b) Use Lagrange Multipliers to find the concentrations (x_A, x_B, x_C) which maximize ΔS_{mix} . Consider appropriate constraints on the concentrations.

$$S = -Mk [x_A \ln x_A + x_B \ln x_B + x_C \ln x_C] \quad g = x_A + x_B + x_C = 1$$

$$\text{LM:} \quad \frac{\partial S}{\partial x_i} - \alpha \frac{\partial g}{\partial x_i} = 0 \quad \text{for all } x_i$$

$$\frac{\partial S}{\partial x_i} = -Mk(1 + \ln x_i) \quad \frac{\partial g}{\partial x_i} = 1 \quad x_i = e^{-1-\alpha/Mk} \quad \text{eliminate } \alpha \text{ by dividing by } \sum_{i=1}^3 x_i = 1$$

$$\rightarrow x_i = \frac{e^{-1-\alpha/Mk}}{\sum_{i=1}^3 e^{-1-\alpha/Mk}} = \frac{e^{-1-\alpha/k}}{3e^{-1-\alpha/k}} = \frac{1}{3} \quad x_A = x_B = x_C = \frac{1}{3}$$

c) If AA, AB, BB, BC, AC, and CC interactions all have the same energy, what is the change of energy of mixing, $\Delta U_{mix}(x_A, x_B, x_C)$?

$$\Delta U_{mix}(x_A, x_B, x_C) = 0$$

d) If AA, AB, BB, BC, AC, and CC interactions all have the same energy, under what conditions will uniform mixing of A, B, and C occur?

Since $\Delta S_{mix}(x_A, x_B, x_C) > 0$, will get uniform mixing under all conditions.

e) Describe a situation, in terms of the interaction energies w_{AA} , w_{AB} , w_{BB} , w_{BC} , w_{AC} , and w_{CC} , where complete mixing of A and B might occur, but C would primarily stay in a separate C rich phase.

If $-w_{CC} \gg -w_{AA}, -w_{AB}, -w_{BB}, -w_{AC}, -w_{BC}$; where all $w_{ij} < 0$.

f) If AA, AB, BB, BC, AC, and CC interactions all have the same energy, find the chemical

potential $\mu_A = \left(\frac{\partial F}{\partial N_A} \right)_{T,V,N_B,N_C}$.

$\Delta U_{mix} = 0$ and $S(pure_A + pure_B + pure_C) = 0$ so

$$F = U - T\Delta S_{mix} = \frac{N_A z w_{AA}}{2} + \frac{N_B z w_{BB}}{2} + \frac{N_C z w_{CC}}{2} + kT [N_A \ln N_A + N_B \ln N_B + N_C \ln N_C - (N_A + N_B + N_C) \ln (N_A + N_B + N_C)]$$

$$\mu_A = \frac{z w_{AA}}{2} + kT \left[1 + \ln N_A - \frac{\partial}{\partial N_A} (N_A + N_B + N_C) \ln (N_A + N_B + N_C) \right]$$

$$\mu_A = \frac{z w_{AA}}{2} + kT [1 + \ln N_A - 1 - \ln (N_A + N_B + N_C)]$$

$$\mu_A = \frac{z w_{AA}}{2} + kT \ln \frac{N_A}{N} = \frac{z w_{AA}}{2} + kT \ln x_A$$

16. Consider the mixing model at $\chi_{AB} = 3$.

a) Find the concentrations x' and x'' which satisfy the common tangent condition to 4 significant digits

$$x' = 0.07072, \quad x'' = 0.9293$$

b) If the imposed total A fraction is $x_0 = 0.4$, what fraction of the system will be in the A rich phase?

$$f = \frac{x_0 - x'}{x'' - x'} = \frac{.4 - 0.07072}{.9293 - .07072} = .3835$$

c) If $N=10000$, how many A and B particles will be in each phase, and how many total particles will be in each phase?

$$N' = (1 - f)N = 6165$$

$$N'' = fN = 3835$$

$$N'_A = x'N' = 436$$

$$N'_B = (1 - x')N' = 5729$$

$$N''_A = x''N'' = 3564$$

$$N''_B = (1 - x'')N'' = 271$$

d) Now add 100 A particles, so $x_0 = 4100/10100 = 0.4059$. How are these new particles distributed between the two phases? Do any other particles move?

$$f = \frac{x_0 - x'}{x'' - x'} = \frac{.4059 - 0.07072}{.9293 - .07072} = .3904$$

$$N' = (1 - f)N = 6156$$

$$N'' = fN = 3944$$

$$N'_A = x'N' = 435$$

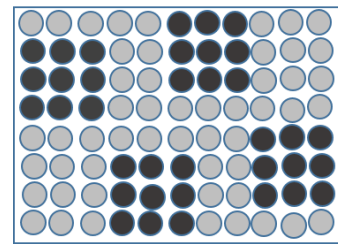
$$N'_B = (1 - x')N' = 5721$$

$$N''_A = x''N'' = 3665$$

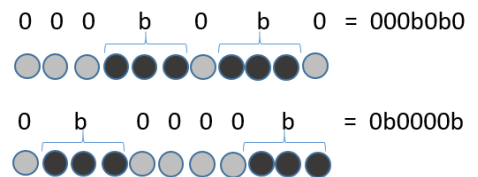
$$N''_B = (1 - x'')N'' = 279$$

So all of the 100 A particles added go into the A rich phase, but at the same time 1 additional A particle goes from the B rich phase into the A rich phase, and 8 B particles move from the B rich phase into the A rich phase. So the A rich phase grows by 109 particles, and the B rich phase shrinks by 9 particles. Don't worry about off by one due to round off.

17. Consider a model of mixing two *unequal* sized molecules using a lattice model. There are N_0 small particles (light gray), each filling one lattice site, and N_b large *rigid* molecules (dark gray), each filling b lattice sites, as shown at right for $b=9$.



To approximately calculate the entropy of this configuration in a simpler geometry, consider a 1D lattice. As shown below right for $b=3$, each possible configuration of this 1D system can be completely specified by a permutation of a string of N_0 0's and N_b b's:



a) Find an expression for the multiplicity, W , of the 1D lattice in terms of N_0 and N_b .

$$W = \frac{(N_0 + N_b)!}{N_0! N_b!}$$

b) Using a), find an expression for the entropy of the mixed system. Simplify using $N_0 \gg 1$ and $N_b \gg 1$ and write in terms of the particle or mole fractions $x_0 = \frac{N_0}{N_0 + N_b}$ and $x_b = \frac{N_b}{N_0 + N_b}$.

$$S = k \ln W = k[(N_0 + N_b) \ln(N_0 + N_b) - (N_0 + N_b) - N_0 \ln N_0 + N_0 - N_b \ln N_b + N_b]$$

$$S = k \ln W = k \left[-N_0 \ln \frac{N_0}{N_0 + N_b} - N_b \ln \frac{N_b}{N_0 + N_b} \right] = -(N_0 + N_b) k [x_0 \ln x_0 + x_b \ln x_b] .$$

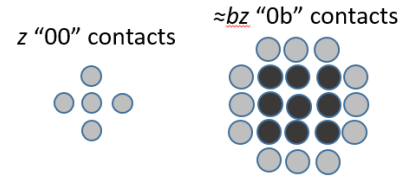
c) Find an expression for the entropy change of mixing $\Delta S_{mix} = S(\text{mixed}) - S(\text{pure } 0) - S(\text{pure } b)$.

$$\Delta S_{mix} = -(N_0 + N_b) k [x_0 \ln x_0 + x_b \ln x_b] .$$

d) Now consider the energy, which can be written as a sum of all “lattice size” contacts, with energy w_{00} , w_{bb} , w_{0b} , depending on whether each lattice face contact is between two small particles, two faces of large particles, or between a face of a large and a small particle, respectively. If we assume that each lattice face contact between small and large particles has the same energy, and if the number of contacts a large molecule makes is (approximately) zb , where z is the coordination number, then $U = m_{00}w_{00} + m_{bb}w_{bb} + m_{0b}w_{0b}$, where the number of lattice face contacts between small particles is:

$$m_{00} = \frac{zN_0 - m_{0b}}{2}, \text{ and the number of lattice face contacts}$$

between large particles is $m_{bb} = \frac{zbN_b - m_{0b}}{2}$. (Each face of a bb contact has b lattice size contacts each with energy w_{bb} . Find an expression for the *change* in energy of mixing under these assumptions in terms of m_{0b} .



$$U_{mix} = \frac{zN_0 - m_{0b}}{2} w_{00} + \frac{zbN_b - m_{0b}}{2} w_{bb} + m_{0b} w_{0b}$$

$$U(\text{pure } 0) = \frac{zN_0}{2} w_{00}$$

$$U(\text{pure } b) = \frac{zbN_b}{2} w_{bb}$$

$$\Delta U_{mix} = \frac{-m_{0b}}{2} w_{00} + \frac{-m_{0b}}{2} w_{bb} + m_{0b} w_{0b} = m_{0b} \left(w_{0b} - \frac{w_{00} + w_{bb}}{2} \right)$$

e) Use the mean field approximation for the large particles, $m_{0b} = zbN_b \frac{N_0}{N_0 + N_b}$, to find an expression for the energy change of mixing $\Delta U_{mix} = U(\text{mixed}) - U(\text{pure } 0) - U(\text{pure } b)$.

$$\Delta U_{mix} = zbN_b \frac{N_0}{N} \left(w_{0b} - \frac{w_{00} + w_{bb}}{2} \right)$$

$$N = N_0 + N_b$$

f) Find an expression for the total Helmholtz free energy change of mixing, $\frac{\Delta F_{mix}}{NkT}$, in terms of x_0 , x_b , and $\chi_{0b} = \frac{z}{kT} \left(w_{0b} - \frac{w_{00} + w_{bb}}{2} \right)$.

$$\Delta U_{mix} = bNkT \chi_{0b} x_0 x_b$$

$$\frac{\Delta F_{mix}}{NkT} = b \chi_{0b} x_0 x_b + x_0 \ln x_0 + x_b \ln x_b$$

g) From f), find an expression for the solubility of low concentrations of large particles (how the maximum soluble x_b depends on χ_{0b}) for small x and large positive χ_{0b} . Compare this two what

you would get from the mixing model for equal sized particles. How does mixing or solubility (under these assumptions) depend on size of the large particle, b ?

Either $\Delta F_{mix} = 0$ or $\frac{\partial F}{\partial x} = 0$ give same approximate solution. $x_0 \approx 1$ $x_b \ll 1$

$$F = b\chi x(1-x) + x \ln x + (1-x) \ln(1-x)$$

$$F' = b\chi(1-2x) + \ln x - \ln(1-x) = 0$$

$$b\chi + \ln x \approx 0$$

$$x_b \approx e^{-b\chi}$$

Compared to equal sized particles, $x \approx e^{-\chi}$, solubility decreases if $b > 1$

h) The solubility of alcohols in water, CH_3OH (methanol), $\text{C}_2\text{H}_5\text{OH}$ (ethanol), $\text{C}_3\text{H}_7\text{OH}$ (propanol), ..., $\text{C}_n\text{H}_{2n+1}\text{OH}$, ... decreases with the length of the carbon chain, n . Does this agree with what you found in part g)? Whether or not it does, which assumption in our model do you think is most deficient for this case, and why?

Solubility decreases with b , in agreement. But assuming that w_{0b} is same for all part of the chain is probably a bad assumption, because alcohol group is water-like ($w_{0b} < 0$) and alkane chain has much higher $w_{0b} \approx 0$.

18. Consider the unfolding of a protein in dilute solution, according to the reaction: $F \rightarrow U$, where F is folded and U is unfolded protein. If this process is modeled as a two-state system with energy levels $\varepsilon_0 = 0$ (folded), and $\varepsilon_1 = \Delta h_0$ (unfolded), find the high temperature limit of the ratio of particles in the two states n_1 / n_0 .

$$\frac{n_1}{n_0} = e^{-\frac{\varepsilon_1 - \varepsilon_0}{kT}} = e^{-\frac{\Delta h^0}{kT}}. \text{ As } T \rightarrow \infty, \frac{n_1}{n_0} \rightarrow 1, \text{ so } n_1 = n_0.$$

19. Consider the equilibrium of a vapor and liquid phase of a pure liquid, and how it depends on p and T .

a) At constant T and p , what is true (besides $dG = 0$) when the number of liquid and vapor molecules are in equilibrium?

$$\mu_{liquid} = \mu_{vapor}$$

b) First, model the liquid as a lattice with $U = m w_{AA}$ and $S = 0$, where $m = zN/2$ is the number of bonds, z is the coordination number of the lattice, and $w_{AA} < 0$ is the energy per bond. What is the chemical potential of the liquid?

$$F_{liquid} = \frac{zNw_{AA}}{2} \quad \mu_{liquid} = \frac{zw_{AA}}{2}$$

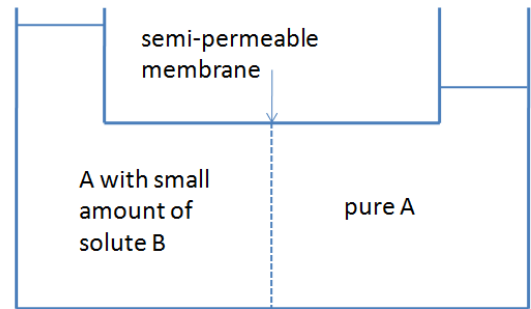
c) What is the chemical potential of the vapor phase (treat as an ideal gas) in terms of p and p_{int}^0 ?

$$\mu_{\text{vapor}} = kT \ln \frac{p}{p_{\text{int}}^0}$$

d) Find the vapor pressure in terms of p_{int}^0 , z , w_{AA} , and kT .

$$\frac{p}{p_{\text{int}}^0} = e^{\frac{zw_{AA}}{2kT}}$$

20. Osmotic pressure. Consider the equilibrium of pure solvent A with a mixture of A and a dilute solute B at fixed Temperature separated by a semipermeable membrane through which solvent molecules can pass, but not solute molecules B. The mixture will be at higher pressure than the pure solvent. This is why red blood cells burst when transferred to pure water (the cell wall is a semipermeable membrane).



a) What is true at equilibrium between the A particles in the mixture on the left of the membrane and the A particles in the pure A phase on the right?

$$\mu_A^{\text{mixture}} = \mu_A^{\text{pure}}$$

b) If a relationship analogous to your expression in part (a) holds for particles of type B, what is it? And if not, why not?

No such relationship exists for B. Particles of type B on the left are not in equilibrium with those on the right.

c) Let the chemical potential of pure A be $\mu_A^{\text{pure}} = \mu_0(T, p)$. The chemical potential of A in the mixture will be $\mu_A^{\text{mixture}} = \mu_0(T, p) + \left(\frac{\partial \mu}{\partial p}\right)_T \Delta p + \Delta \mu_A^{\text{mix}}$, modified by an increase in pressure and a change of chemical potential due to the entropy of mixing. Derive a Maxwell relation for $\left(\frac{\partial \mu}{\partial p}\right)_{T,N}$ and write it terms of the molar volume of A in the mixture phase. Assume that v_A is independent of p (a pretty good assumption).

$$\left(\frac{\partial \mu}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial N}\right)_{T,p} = v_A$$

d) Since $\Delta \mu_A^{\text{mix}}$ in the regular solution model is given by $\Delta \mu_A^{\text{mix}} = kT \ln x_A$, where $x_A = N_A/N$, is the fraction of A molecules in the mixture phase, use a) and b) to solve for the pressure difference Δp in terms of $x_B = N_B/N$ and v_A .

$$\mu_A^{\text{mixture}} = \mu_A^{\text{pure}}$$

$$\mu^0 + \left(\frac{\partial \mu}{\partial p}\right)_T \Delta p + \Delta \mu_{\text{mix}} = \mu^0$$

$$v_A \Delta p + kT \ln x_A = 0$$

$$\Delta p = -\frac{kT \ln x_A}{v_A} = -\frac{kT \ln(1-x_B)}{v_A} \approx \frac{kT x_B}{v_A}$$

e) Now consider a situation where the membrane is very slightly permeable to the singly charged positive ions of A, (A^+), but is impermeable to the negatively charged ions of A (A^-), because they are larger. If the potential of the solution on the left side of the membrane is 118.4mV lower than the potential on the right side at 298K, what is the ratio of the A^+ ion concentrations on the left and right side of the membrane, $[A^+]_{\text{left}}/[A^+]_{\text{right}}$?

$$\Delta V = 118.4 = \frac{kT}{e} \ln \left[\frac{A^+_{\text{left}}}{A^+_{\text{right}}} \right]$$

$$\left[\frac{A^+_{\text{left}}}{A^+_{\text{right}}} \right] = e^{\frac{118.4 \cdot 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \cdot 298}} = e^{4.607} = 100.2$$

21. Mixing. Consider a model of mixing two equal sized molecules of type A and B, where the free energy of mixing (the free energy of a uniform mixture of A and B relative to pure A + pure B) is given by $\Delta F_{\text{mix}} = \sin^2 \pi x - c \sin \pi x$, where x is the mole fraction of A, $1-x$ is the mole fraction of B, and c is a parameter that varies with temperature and can be positive or negative. This model is similar to the regular solution model of mixing, but has some important differences. ΔF_{mix} for four representative values of c is shown at right (0,1, $\sqrt{2}$,2). You must give mathematical justifications for all parts below.

a) If the system separates into two phases with $0 < x', x'' < 1$, what condition is satisfied at x' and x'' ? Use $\Delta F_{\text{mix}} = \sin^2 \pi x - c \sin \pi x$ to evaluate this condition.

$$F' = 2\pi \sin \pi x \cos \pi x - c \pi \cos \pi x = 0$$

$$c = 2 \sin \pi x$$

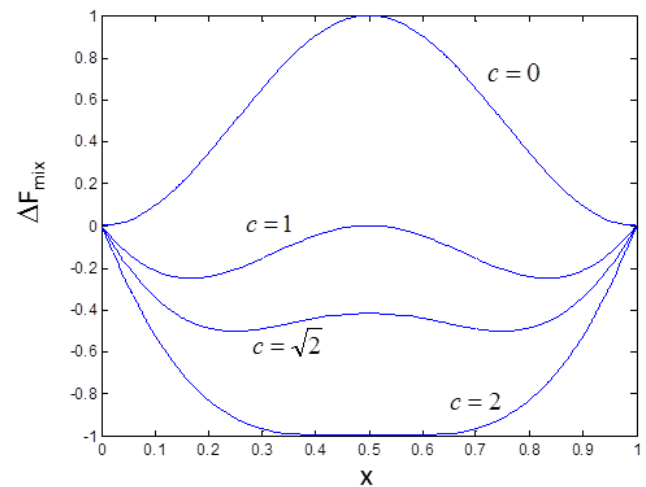
b) If the system is metastable when uniformly mixed at x_0 , what condition is satisfied? Use

$$\Delta F_{\text{mix}} = \sin^2 \pi x - c \sin \pi x \text{ to evaluate this condition.}$$

$$F'' = 2\pi^2 (\cos^2 \pi x - \sin^2 \pi x) + c \pi^2 \sin \pi x > 0$$

c) If $c = \sqrt{2}$ and equal amounts of A and B are uniformly mixed and then allowed to approach equilibrium, does the system spontaneously separate into phases? If the system separates, find the mole fraction of A in each phase, and the fraction of the system in each phase.

Yes, $x' = 1/4$, $x'' = 3/4$ $f = (.5 - .25)/(.75 - .25) = 1/2$



d) If $c = \sqrt{2}$ and the initial uniform mixture has mole fraction $x_0=0.4$, does the system spontaneously separate into two phases? If so find the mole fraction of A in each phase and the fraction of the system in each phase.

Yes, $x'=1/4$, $x''=3/4$ $f=(.4-.25)/(.75-.25)=0.3$

e) If $c = \sqrt{2}$ and the initial uniform mixture has mole fraction $x_0 = 1/\pi$, does the system spontaneously separate into two phases? If so find the mole fraction of A in each phase and the fraction of the system in each phase.

$x_0=1/\pi > x'=0.25$, but $F''=3.531 > 0$ metastable, does not spontaneously separate

f) If $c = \sqrt{2}$ and the initial mixture has mole fraction $x_0=0.1$, does the system spontaneously separate into two phases? If so find the mole fraction of A in each phase and the fraction of the system in each phase.

$x_0=0.1 < x'=0.25$, does not separate

g) Uniformly mix 4000 particles of A and 6000 particles of B at $c = \sqrt{2}$ and then allow them to separate if they do so spontaneously. What are the numbers of particles of type A and B in each phase?

$x_0=0.4$, separates, $f=0.3$ at $x''=0.75$; $1-f=0.7$ at $x'=0.25$

$N'=7000$ $N''=3000$

$N_A'=1750$ $N_B'=5250$

$N_A''=2250$ $N_B''=750$

h) Now construct a phase diagram for this system as a function of c and x_0 (the imposed total mole fraction of A) on the axes below. Derive and clearly label equations, $c(x)$, for the spinoidal (metastability) boundary (if it exists), any binoidal (global stability) boundaries, and on the graph clearly label any regions of uniform mixing, 2 partially mixed phases, 2 pure A and B phases, and metastable regions.

