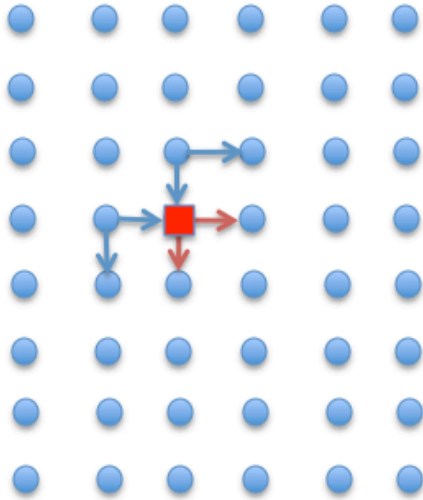


Problem 1 (25 Points) Lattice Models, again..... ☹..... ☺

Condensed phases (liquid, solids) have historically been treated as lattice models. In this case, consider a bulk liquid as a lattice site model. There are N particles, and the particles interact with a nearest-neighbor pair-wise interaction that leads to an energy contribution of 'w' to the total internal energy, U , of the system from a pair of particles interacting. In this lattice model, the number of nearest neighbors for any particle in the bulk (neglect the edges) is 'z'. For an N -particle system, the total internal energy from interactions is $U_{\text{interaction}} = \frac{1}{2} Nzw$. The per-particle interaction contribution to U is thus $\frac{U_{\text{interaction}}}{N} = \frac{1}{2} zw$. It is important to note that this type of interaction implicitly builds in a reference state where the particles do not interact (i.e. 'large' separation, or 'dilute' conditions); in such a reference state, $U_{\text{interaction}} = 0$ (much like in the case of an ideal gas). In the lattice, dynamic effects are taken into account since the lattice is an 'average' representation of the positions of particles. All lattice sites are filled, and the particles are indistinguishable.



Edge effects neglected

Particle-Particle interaction energy = w

Nearest neighbors of a particle = z

Total internal energy arising from particle-particle interactions in an N -particle system

$$U_{\text{interaction}} = \frac{1}{2} Nzw$$

(this expression for U avoids double counting the energy interactions by ascribing $z/2$ of the interactions to each particle

A. (5 Points). Using the definition of the Helmholtz Free Energy, please provide an appropriate equation for this thermodynamic quantity for this lattice model liquid based on the given information and in terms of the variables presented in the above discussion and associated figure.

$$\begin{aligned} A(T,V,N) &\equiv U - TS = U_{\text{interaction}} - TS = U_{\text{interaction}} - T(k_B \ln(W)) \\ &= U_{\text{interaction}} - T\left(k_B \ln\left(\frac{N!}{(N!)(0!)}\right)\right) = U_{\text{interaction}} - T(k_B \ln(1)) = U_{\text{interaction}} \\ A(T,V,N) &= \frac{1}{2} Nzw \end{aligned}$$

B. (5 Points). Using the definition of the chemical potential, please provide an appropriate equation for this thermodynamic quantity.

$$\mu_{\text{liquid}} = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \left(\frac{\partial (\frac{1}{2} Nzw)}{\partial N}\right)_{T,V} = \frac{1}{2} zw$$

C (5 Points). Using the results from Parts A and B and your knowledge of the chemical potential of a pure ideal gas, determine a relation between the vapor pressure of the liquid and the interaction strength, 'w'. You are free to define the reference state ideal gas chemical potential to be 0.

Since this question asks about vapor pressure, we think of vapor - liquid equilibrium. At conditions of vapor - liquid equilibrium, we know that vapor and liquid chemical potentials are equal.

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

We have computed the liquid chemical potential (for lattice model liquid) in Part B. For ideal gas, we know the behavior of chemical potential as a function of pressure :

$$\mu_{ideal,vapor} = \mu^{ref} + RT \ln\left(\frac{p}{p^{ref}}\right)$$

Equating chemical potentials gives :

$$\frac{1}{2} z w = \mu^{ref} + RT \ln\left(\frac{p}{p^{ref}}\right)$$

Feeling free to set the reference state ideal gas chemical potential to 0:

$$\frac{1}{2} z w = RT \ln\left(\frac{p}{p^{ref}}\right)$$

Rearranging :

$$p = p^{ref} e^{\frac{z w}{2RT}}$$

D1. (5 Points). The vapor pressure of water is 22 mmHg at $T = 300\text{K}$ and 760 mmHg at $T = 373\text{K}$. Estimate the vaporization enthalpy using appropriate analytics.

This is a Clausius-Clapeyron analysis. Assume vaporization enthalpy is constant over the temperature and pressure ranges probed, and liquid is transferred to an ideal vapor phase:

$$\ln\left(\frac{p_2}{p_1}\right) = \frac{-\Delta h_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\Delta h_{\text{vap}} = -R \ln\left(\frac{p_2}{p_1}\right) \left(\frac{1}{T_2} - \frac{1}{T_1}\right)^{-1}$$

$$= -(8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \ln\left(\frac{760 \text{ mmHg}}{22 \text{ mmHg}}\right) \left(\frac{1}{373 \text{ K}} - \frac{1}{300 \text{ K}}\right)^{-1}$$

$$\Delta h_{\text{vap}} = 45.14 \text{ kJ mol}^{-1}$$

D2. (5 Points). What is an estimate of the interaction strength 'w' considering water to be modeled as a lattice fluid? Consider $z = 4$ for a lattice model of water. Refer to your analyses of Parts A through E for inspiration.

S1: In this approach, we compare the differential forms of the vapor pressure expressions we have derived and have at our disposal:

From Clausius - Clapeyron Analysis

$$d(\ln P) = \left(\frac{\Delta h_{\text{vap}}}{R}\right) \left(\frac{1}{T^2}\right) dT$$

From Analysis of Part 1C :

$$d(\ln P) = \left(\frac{-zw}{2R}\right) \left(\frac{1}{T^2}\right) dT$$

Comparing the expressions, we have :

$$\left(\frac{-zw}{2R}\right) = \left(\frac{\Delta h_{\text{vap}}}{R}\right)$$

$$w = \left(\frac{-2\Delta h_{\text{vap}}}{z}\right)$$

$$= \left(\frac{-2(45.14 \text{ kJ mol}^{-1})}{4}\right) = -22.57 \text{ kJ mol}^{-1} = -5.4 \text{ kcal mol}^{-1}$$

S2. If we think of vaporization as a molecule moving from the condensed phase (liquid) to the ideal vapor (where there are no interactions between particles), then the vaporization enthalpy corresponds to the loss of interaction per particle on a mole basis. This is simply the interaction contribution of a single particle to the potential energy of the liquid, and so:

$$(\Delta h_{vap}) = U_{final} - U_{init} = 0 - U_{init} = \left(\frac{-z w}{2} \right)$$

$$w = \left(\frac{-2 \Delta h_{vap}}{z} \right)$$

$$= \left(\frac{-2(45.14 \text{ kJ mol}^{-1})}{4} \right) = -22.57 \text{ kJ mol}^{-1} = -5.4 \text{ kcal mol}^{-1}$$

Problem 2 (15 Points) Multiple Choice? Why yes.....

For the following, match the statement in the left-hand side column with the most appropriate **answer(s)** from the right-hand side column.

I. Under the Ehrenfest classification scheme, a first-order phase transition is one in which the Gibbs Free Energy changes continuously (smoothly) and properties related to first derivatives of G change discontinuously. The pure substance liquid-vapor phase transition is first-order, true or false? <u> B </u>	A. ∞ (diverges)
	B. true
II. How many intensive degrees of freedom are available for a system comprised of a binary liquid solution in equilibrium with its vapor (both species present in both phases)? <u> P </u> .	C. false
	D. greater than 0
	E. equal to 0
III. Negative absolute temperatures arise under particular conditions, such as: <u> N,Q </u>	F. 1
	G. $\sum_j \nu_j \mu_j = 0$
	H. entropy
	I. isenthalpic
IV. What is the theoretical value of $C_p(T)$ at the liquid-vapor phase transition temperature? <u> A </u>	J. 0 J/K
	K. 3
V. The Legendre Transform of $U(S,V,N)$ to a function of T,V,N results in what thermodynamic potential? <u> S </u>	L. 4
	M. internal energy
VI. The maximum non-expansion work related to a transformation (under conditions of equilibrium along the process) of a chemical system between two equilibrium thermodynamic states is equal to <u> T </u> . Consider the process to occur with external temperature and pressure constraints (values are constant).	N. relatively few quantum states available/accessible at a particular temperature
VII. The Gibbs Free Energy of mixing of two ideal gases, A and B, is identically zero (due to ideality of the vapor phase species). True or False? <u> C </u>	O. $T dQ$
	P. 2
VIII. For a binary mixture of ideal gases at constant temperature and pressure, what mole fraction ratio would maximize the entropy of the system? <u> F </u>	Q. population inversion of quantum states
	R. q is isentropic
IX. What constraint arises when there is a reversible (equilibrium) chemical reaction? <u> G </u> .	S. Helmholtz Free Energy
X. In a two-state system (i.e., 2 energy levels, 'high' and 'low') with 10 non-interacting particles what value would represent the ratio of occupancies of the two states (or equivalently, what value would represent the ratio of 'high' to 'low' labeled particles)? <u> F </u>	T. Gibbs Free Energy

Problem 3 (20 Points) Put me to sleep already.....

A common anesthetic drug molecule is halothane (2-bromo-2-chloro-1,1,1-trifluoroethane). Its mode of action is presumed to involve partitioning from water (state A) into lipid bilayer membranes (state B). The values of the equilibrium constant representing this reversible partitioning, determined at two different pressures, are the following:

P (atm)	0	280
ln K	7.84	7.6
T (Kelvin)	300	300

What is the corresponding change in molar volume of the bilayer/water/drug system as a result of the pressure change from $p_1 = 0 \text{ atm}$ to $p_2 = 280 \text{ atm}$?

Solution:

$$\Delta \bar{G}_{rxn} = -RT \ln K$$

At constant T (data given at $T = 300\text{K} = \text{constant}$)

$$d \ln K = \frac{-d(\Delta \bar{G}_{rxn})_T}{RT} = \frac{-1}{RT} (\Delta \bar{V}_{rxn} dP - \Delta \bar{S}_{rxn} dT)$$

$$d \ln K = \frac{-1}{RT} (\Delta \bar{V}_{rxn} dP)$$

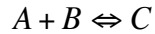
$$\Delta \bar{V}_{rxn} = -RT \left(\frac{\partial \ln K}{\partial P} \right)_T$$

Assume change in V is constant; use a constant slope approximation from data given :

$$\begin{aligned} \Delta \bar{V}_{rxn} &\approx -(8.314 \text{ J mol}^{-1} \text{ K})(300 \text{ K}) \left(\frac{\Delta \ln K}{\Delta P} \right)_T \\ &= -(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(300 \text{ K}) \left(\frac{(7.6 - 7.84)}{(280 \text{ atm} - 0 \text{ atm})} \right)_T \\ &= 0.021 \text{ L/mol} \\ &= 21 \text{ cm}^3 / \text{mol} \end{aligned}$$

Problem 4 (20 Points) What are Legendre Transforms Good For Anyway.....

Here we will consider the utility of Legendre Transforms in determining useful thermodynamic potentials that reach extrema under conditions of chemical equilibrium with constant pressure, temperature, and **chemical potential**. That is, in order to use, as a *control* 'knob', a species chemical potential, we need to determine what thermodynamic potential depends on the chemical potential of interest. This is not an irrelevant question to ask, since biochemical reactions often occur under conditions of constant pH, where the concentration of proton is controlled (specified). Knowing that chemical potentials, in appropriate limits can be expressed in terms of concentrations, constant pH scenario is a case of constant proton chemical potential. Let's consider a simple equilibrium (reversible) reaction:



A. (1 Points) Because of chemical equilibrium, what constraint arises involving species chemical potentials (recall the discussion of ideal gas reaction equilibrium, though in this exercise, we are considering a general situation).

$$\sum_j \nu_j \mu_j = 0$$

B. (1 Points) Without taking into account your constraint, write down the total differential of the extensive Gibbs Free Energy (knowing that Gibbs Free Energy is a function of T, P, and the amounts of species, A, B, C). Be careful and provide the complete expression. Use the nomenclature: n_i =moles of species 'i' and ' μ_i ' is chemical potential of species 'i'.

$$dG(T, P, \{n_j\}) = VdP - SdT + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C$$

C. (5 Points) Using your constraint from Part A, eliminate the chemical potential of species C from your results of Part B. You can make the substitution:

$$n'_A = n_A + n_C; \quad dn'_A = dn_A + dn_C; \quad n'_B = n_B + n_C; \quad dn'_B = dn_B + dn_C.$$

These substitutions are another way to say that A is 'distributed' between free A and 'bound' A that has transformed to species C; similarly for species B.

Chemical reaction equilibrium constraint :

$$\mu_A + \mu_B = \mu_C$$

Thus :

$$\begin{aligned} dG(T, P, \{n_j\}) &= VdP - SdT + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C \\ &= VdP - SdT + \mu_A dn_A + \mu_B dn_B + (\mu_A + \mu_B) dn_C \\ &= VdP - SdT + \mu_A (dn_A + dn_C) + \mu_B (dn_B + dn_C) \\ &= VdP - SdT + \mu_A dn'_A + \mu_B dn'_B \end{aligned}$$

D. (3 Points) Based on your results of Part C, what are the variables that G really depends on? Excluding temperature and pressure, there are 2 (two).

$$dG = VdP - SdT + \mu_A dn'_A + \mu_B dn'_B$$

Thus :

$$dn'_A \text{ and } dn'_B$$

E. (7 Points) Now, we want to control the chemical potential of species B in our reaction----that is, we want to specify the value of μ_B . Provide a Legendre transform of the Gibbs Free Energy (the thermodynamic potential you have been working with so far in Parts A- D) to another thermodynamic potential, G' , that would leave you with μ_B as one of the independent variables. Show that indeed the new potential you generated is in part dependent on μ_B .

$$G' = G - \left(\frac{\partial G}{\partial n'_B} \right) n'_B \quad \text{new potential defined by Legendre transform}$$

To show that the new potential is indeed dependent on μ_B :

$$G' = G - \left(\frac{\partial G}{\partial n'_B} \right) n'_B = G - \mu_B n'_B \quad \text{new potential defined by Legendre transform}$$

$$dG' = dG - d(\mu_B n'_B) = VdP - SdT + \mu_A dn'_A + \mu_B dn'_B - \mu_B dn'_B - n'_B d\mu_B$$

$$dG' = VdP - SdT + \mu_A dn'_A - n'_B d\mu_B$$

The last expression shows that G' is dependent on μ_B

F. (3 Points) At constant temperature, pressure, and μ_B , what does the total differential of G' become in terms of μ_A and dn'_A ? That is, what is $(dG')_{T,P,\mu_B}$? What is the integrated form of G' and what variables does G' depend on?

$$dG' = \mu_A dn'_A$$

Integrated form :

$$G' = \mu_A n'_A$$

Problem 5 (20 Points) It's bubblicious.....

For the binary system acetonitrile(1)/nitromethane(2), liquid-vapor equilibrium is adequately represented through Raoult's expression. Antoine equations for saturation pressures as a function of temperature (in Celsius) are:

$$\ln(P_1^{sat}) = 14.2724 - \frac{2945.47}{t + 224.0} ; \ln(P_2^{sat}) = 14.2043 - \frac{2972.64}{t + 209.0}$$

What is the bubble temperature at P = 70 kPa and initial composition of 0.6 mole fraction of acetonitrile at initial temperature t = 90 Celsius.

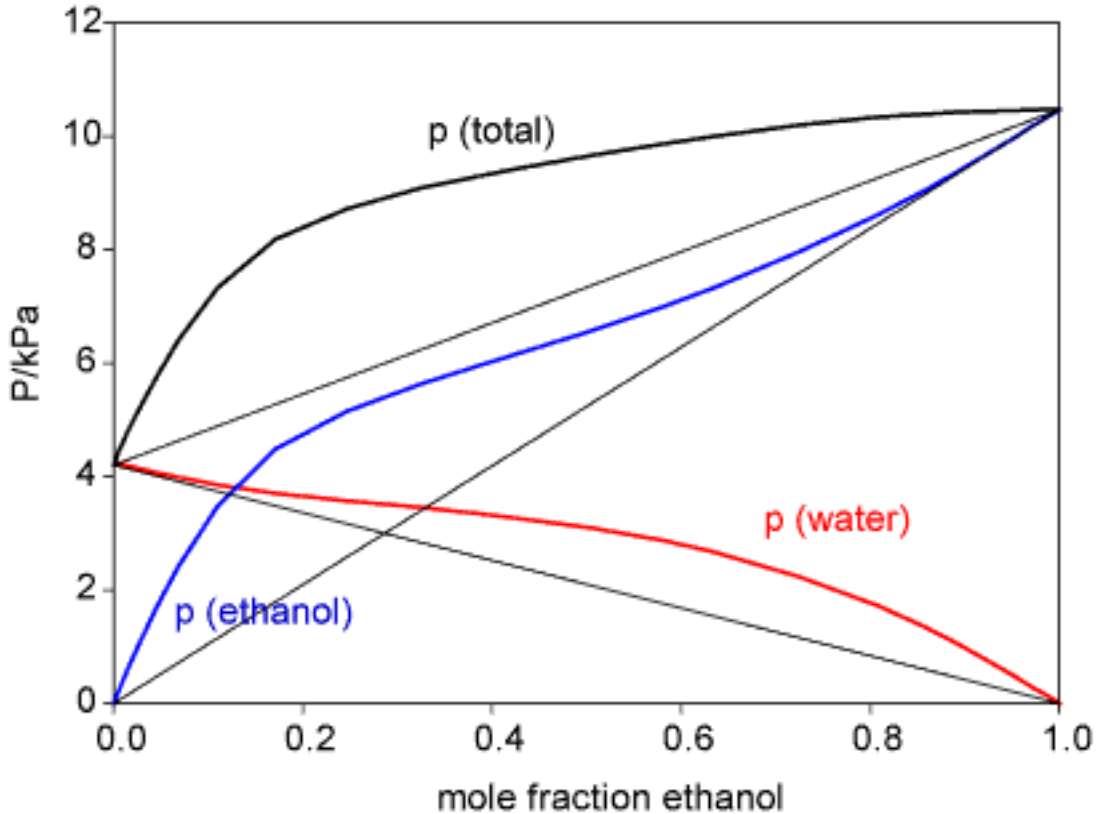
This is best done via iterating over the total pressure. The liquid phase composition at the bubble temperature is x1=0.6 and x2=0.4. We plot in the last column the relative error in our predicted total Pressure. The last temperature gives a fairly low relative error, and we state that value as our solution.

$$P^{total} = x_1 P_1^{sat} + x_2 P_2^{sat}$$

$$relative\ error = \frac{P_{predicted}^{total}}{P^{total}}$$

P	t	(x1)(P1sat)	(x2)(P2sat)	diff/P
				-
70	100	106.7636578	39.16623773	1.084712794
				-
70	90	79.92563735	28.39092264	0.547379428
				-
70	80	58.70520086	20.12690971	0.126173008
70	70	42.22316204	13.92082071	0.197943104
70	75	49.92411448	16.79308198	0.046897193
70	75.5	50.75194804	17.10485805	0.030617056
70	76	51.59068036	17.42129796	0.014114595
				-
70	76.5	52.44041316	17.7424528	0.002612371
70	76.4	52.26958166	17.67784218	0.000751088
70	76.42	52.30371247	17.69074907	7.91208E-05

Problem 6. Extra Credit (5 Points) Time to jam.....



In this figure, the y-axis represents the vapor pressure of the solution of an ethanol-water. Straight lines are the vapor phase partial pressures based on Raoult's equation. Treating the vapor as ideal and still considering the liquid solution as non-ideal, what thermodynamic quantity related to the species in the liquid is also being plotted on the y-axis. Please show your work in order to receive credit.

Solution:

On the y-axis, we are plotting partial pressures of the species in the ideal gas vapor mixture. If we consider the fugacities of the species in vapor and liquid, we come to the following conclusion:

$$\hat{f}_i^{vapor} = \hat{f}_i^{liquid}$$

$$\hat{f}_i^{vapor} = \hat{\phi}_i^{vapor} p_i = (1)y_i P^{total} \quad \text{fugacity coefficient} = 1 \text{ for ideal vapor}$$

Thus

$$\hat{f}_i^{liquid} = p_i$$

The y-axis plots the liquid phase fugacity of species 'i'.

Potentially Useful Information

Stirling's Approximation:

$$\ln(N!) = (N \ln N) - N \quad N \rightarrow \infty$$

$N_A R = k_B =$ Boltzmann Constant

Number of ways to place N indistinguishable objects into M bins:

$$W = \frac{M!}{N!(M-N)!}$$

$S = k_B \ln(W)$ (isolated system, statistical mechanical form of entropy for lattice model)

$$\mu_i = f_i$$

$$d\mu = RTdp$$

$$\hat{f}_i^{vapor} = \hat{\phi}_i^{vapor} p_i = y_i P^{total}$$

$$\mu(T, P\{x\}) = \mu_{still}^{ref} + RT \ln(\gamma c_i)$$

$$d\mu = RTdp$$

$$du = PRdT + \mu_{still}^{ref} + \nabla \cdot$$

$$\hat{f}_i^{vapor} = \hat{f}_i^{liquid} \quad (\text{at mixture vapor - liquid equilibrium})$$

$$\mu(T, P\{x\}) = \mu_{still}^{ref} + RT \ln(\phi c_i)$$

NAME: _____
Section Number: 10

CHEMISTRY 443, Fall, 2014 (14F)
Examination 1, October 1, 2014

Answer each question in the space provided; use back of page if extra space is needed. Answer questions so the grader can READILY understand your work; only work on the exam sheet will be considered. Clearly indicate your answer and all indications of your logic in arriving at your answer. Please answer the question asked and refrain from providing irrelevant comments or information. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.

DO NOT WRITE IN THIS SPACE
p. 1 _____ /25
p. 2 _____ /15
p. 3 _____ /20
p. 4 _____ /20
p. 5 _____ /20
=====
p. 6 _____ /5 (Extra credit)
=====
TOTAL PTS
/100