

NAME: \_\_\_\_\_  
Section Number: 10

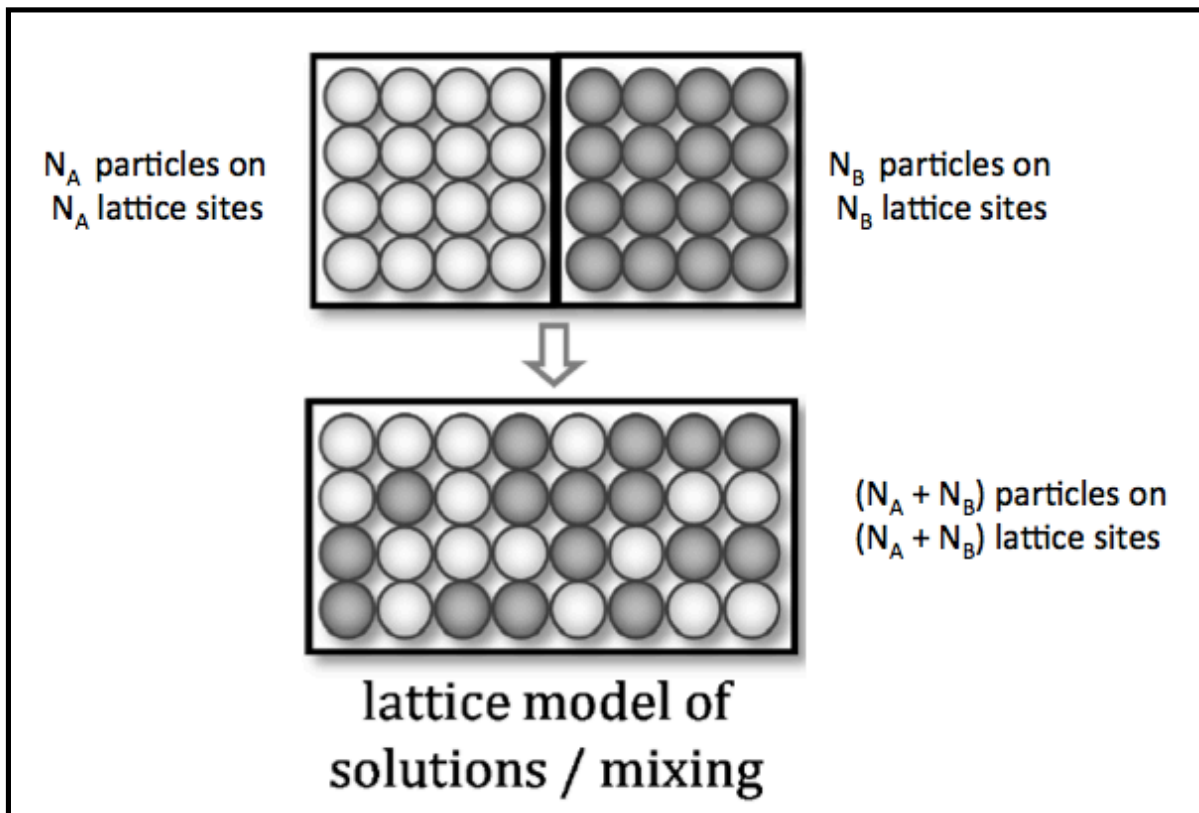
CHEMISTRY 443, Fall, 2014 (14F)  
Examination 1, October 1, 2014

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. Potentially useful information is provided on Page 10. Write answers, where appropriate, with reasonable numbers of significant figures. You may use **only** the "Student Handbook," a calculator, and a straight edge.

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

### Problem 1 (20 Points) Lattice Models and Ideal Mixing

Lattice models have found a broad range of application as models for physical processes involved with protein folding, phase transitions, protein-ligand binding, understanding surface adsorption isotherms (i.e. Langmuir isotherm), among many others. Here we consider a lattice solution model to obtain the entropy of mixing of ideal liquids, A and B. In this case, the interactions between A-A particles and B-B particles are considered to be of the same magnitude as A-B, thus effectively precluding preferential interactions of homo-dimers. This is a renormalized way of constituting an ideal system that includes interactions. We need to find the entropy change of mixing for this lattice solution. The initial state is one where  $N_A$  indistinguishable particles are arranged on  $N_A$  sites of a lattice;  $N_B$  indistinguishable particles of liquid B are arranged on  $N_B$  lattice sites (shown in figure). After mixing, all particles are found in the total sites initially available. There are no empty lattice sites either before or after the mixing. Using your knowledge of thermodynamics and combinatorics, determine an expression for the mixing entropy of these ideal liquids. Consider the thermodynamic limit ( $N_i \rightarrow \infty$ ). Your final answer **must** be in terms of mole fractions of species A and B.



**Solution:**

$$\begin{aligned}
\Delta S &= S_{final} - S_{initial} = S_{mix} - S_A - S_B \\
&= k_B [\ln(W_{mix}) - \ln(W_B) - \ln(W_A)] \\
&= k_B \left[ \ln \left( \frac{(N_A + N_B)!}{N_A! N_B!} \right) - \ln \left( \frac{(N_A)!}{N_A! 0!} \right) - \ln \left( \frac{(N_B)!}{0! N_B!} \right) \right] \\
&= k_B \left[ \ln \left( \frac{(N_A + N_B)!}{N_A! N_B!} \right) - \ln(1) - \ln(1) \right] = k_B \left[ \ln \left( \frac{(N_A + N_B)!}{N_A! N_B!} \right) \right]
\end{aligned}$$

*Apply Stirling's Approx.*

$$\begin{aligned}
\Delta S &= k_B [\ln((N_A + N_B)!) - \ln((N_A)!) - \ln((N_B)!)] \\
&= k_B [(N_A + N_B) \ln(N_A + N_B) - (N_A + N_B) - N_A \ln(N_A) + N_A - N_B \ln(N_B) + N_B] \\
&= k_B [(N_A + N_B) \ln(N_A + N_B) - N_A \ln(N_A) - N_B \ln(N_B)] \\
&= k_B [(N_A) \ln(N_A + N_B) + (N_B) \ln(N_A + N_B) - N_A \ln(N_A) - N_B \ln(N_B)] \\
&= k_B [(N_A) \ln(N_A + N_B) + (N_B) \ln(N_A + N_B) - N_A \ln(N_A) - N_B \ln(N_B)] \\
&= -k_B \left[ (N_A) \ln \left( \frac{N_A}{N_A + N_B} \right) + (N_B) \ln \left( \frac{N_B}{N_A + N_B} \right) \right] \\
&= -Nk_B [(x_A) \ln(x_A) + (x_B) \ln(x_B)]
\end{aligned}$$

**Problem 2 (20 Points)** 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. The First 'Law' guarantees full conversion of heat to work during a cyclically-operating process. True or False? <u>      <b>B</b>      </u>	A. isentropic
	B. true
II. Enthalpy of an ideal gas depends on <u>      <b>N</b>      </u> .	C. false
	D. greater than 0
	E. equal to 0
III. The entropy change of the universe for an adiabatic, irreversible process is <u>      <b>D</b>      </u>	F. less than 0
	G. enthalpy
	H. entropy
	I. isenthalpic
IV. What function of pressure and volume is constant along a reversible adiabat of a fluid described by the EOS: $PV=nRT$ ( $n$ = moles)? <u>      <b>O,H</b>      </u>	J. 2
	K. 3
V. Entropy is an extensive state function. True or False? <u>      <b>B</b>      </u>	L. 4
	M. internal energy
VI. An ideal gas is contained in a vessel divided into two compartments initially separated by an impermeable barrier; the vessel is rigid and insulated. The barrier can move to accommodate the pressures in the individual compartments. The barrier is diathermal. The barrier is removed after the initial systems have equilibrated. The entropy change of the system (i.e. gas) for this adiabatic process is <u>      <b>E or U or both</b>      </u>	N. temperature
VII. To completely describe macroscopically a pure, single-phase fluid, the amount and <u>      <b>J</b>      </u> independently-variable properties are required.	O. $PV^\gamma$
	P. irreversible
VIII. For an ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = ?$ <u>      <b>U or E or both</b>      </u> ( $U$ = internal energy)	Q. enthalpy is a state function
	R. $q$ is isentropic
IX. The Joule-Thomson Process is described as <u>      <b>P,I</b>      </u> .	S. enthalpy is path dependent
X. Hess' 'Law' is a restatement of the property that <u>      <b>Q</b>      </u> .	T. yes!
	U. zero

### Problem 3 (20 Points) The Thermo of Electrostatics

In this problem, we will consider energetics associated with electrostatics. Chemists and biochemists often invoke the notion of **point** (partial) charges to describe interactions between molecules (this is a classical treatment of matter as compared to a quantum mechanical picture which is treated in CHEM44). Let's consider the reversible work associated with creating a spherical volume of radius 'a' with total charge  $Q_{\text{final}}$  uniformly and continuously dispersed within that volume. The charge density (charge per volume) is taken to be constant and called  $\rho$ . The constancy of charge density means that regardless of the size of the spherical volume, the amount of charge dispersed within the sphere is such that the charge density is always  $\rho$ . Due to the spherical symmetry of the problem, the way we will consider building up to total charge  $Q_{\text{final}}$  in the sphere is by forming infinitesimally thin layers (or shells if you prefer) around the center of the sphere (located at Cartesian coordinates  $x=y=z=0$ ); the thin layers are defined between  $r$  and  $r+dr$  with  $r$  being the radial distance from the center of the sphere. We will add an infinitesimal amount of charge  $dQ$  within each layer by bringing  $dQ$  from a large distance away ( $r=\text{infinity}$ ) into the thin, spherical shell/layer. If  $Q(r)$  is the charge in the sphere when the sphere has attained radius  $r$ , then the work done in bringing a charge  $dQ$  to it is:

$$dW = \frac{1}{4\pi\epsilon_o} \frac{Q(r)}{r} dQ$$

Remember that this is done in the absence of any heat interactions, is reversible, and that the amount of charge in the sphere at any size of radius (during the growing process) can be determined in terms of the constant charge density and available geometric properties of the system; for

instance,  $Q_{\text{final}} = \frac{4}{3}\pi a^3 \rho$ .

**3A.** What is the total reversible work needed to build up the sphere from radius 0 to radius 'a'? Please provide your answer in terms of 'a' and  $Q_{\text{final}}$ .

Solution:

$$dW = \frac{1}{4\pi\epsilon_o} \frac{Q(r)}{r} dQ$$

$$Q(r) = \rho \left( \frac{4}{3}\pi \right) r^3$$

$$dQ = 4\pi\rho r^2 dr$$

$$dW = \frac{4\pi}{3\epsilon_o} \rho^2 r^4 dr$$

$$W = \frac{4\pi}{3\epsilon_o} \rho^2 \int_{r=0}^{r=a} r^4 dr = \frac{4\pi}{15\epsilon_o} \rho^2 a^5$$

$$\rho^2 = \left( \frac{3Q_{\text{final}}}{4\pi a^3} \right)^2$$

$$W = \frac{3}{5} \frac{Q_{\text{final}}^2}{4\epsilon_o \pi a}$$

**3B.** Based on your answer to Part **3A**, determine the amount of reversible work involved as this charge distribution becomes a true **point charge**. State any assumptions or limiting conditions you invoke in your response.

Solution:

Take the limit of the result from Part 3A as the sphere radius goes to 0. this is the limiting condition for taking the spherical volume to a point.

$$W = \frac{3 Q_{final}^2}{5 4 \epsilon_0 \pi a} \rightarrow \infty \quad a \rightarrow 0$$

This suggests a dilemma since the work cannot be infinite in order to create a single point charge, let alone create an assembly of point charges that can interact.

**3C.** What is the potential energy of this point charge?

From the First 'Law', the reversible work in this case is equal to the change in potential energy. If we take the reference potential energy as no charge in the volume, then the potential energy becomes the reversible work. The potential energy is infinite.

$$U_{potential} = W = \frac{3 Q_{final}^2}{5 4 \epsilon_0 \pi a} \rightarrow \infty \quad a \rightarrow 0$$

**3D.** What is the potential energy of a configuration of point charges (i.e., a molecule defined classically, a protein in solution described by having point charges, etc.)? Discuss your answer/result with some relevant comments.

$$U_{potential} = W = \frac{3 Q_{final}^2}{5 4 \epsilon_0 \pi a} \rightarrow \infty \quad a \rightarrow 0$$

This result is a consequence of the result of par b, which effectively states that the self-energy (the energy involved in just creating the point charge somewhere in space) of a collection of charges is infinite. This suggests that the idea of locating charge at a point and then using the point distribution for obtaining electrostatic fields and potentials (i.e. the Coulomb potential) is inconsistent. This suggests that perhaps we need to always consider some distribution of charge over a finite volume in space. Unfortunately, quantum mechanical treatments of electromagnetism encounter these same infinite self-energies of electrons! Fortunately, physicists have worked out a prescription called renormalization that avoids the infinities.

**Problem 4 (20 Points) The First Law**

**4A.** How much heat is required to increase the temperature of nitrogen (1 kg) from -20 Celsius to 100 Celsius via constant pressure process?  $\bar{C}_V = 5 \frac{\text{cal}}{\text{mol} \cdot ^\circ\text{C}}$  ;  $R = 2 \frac{\text{cal}}{\text{mol} \cdot ^\circ\text{C}}$

Solution:

$$\begin{aligned} q &= n(\bar{C}_V + R)\Delta T \\ &= \left( \frac{1000 \text{ gram}}{28 \text{ gr/mole}} \right) \left( 5 \frac{\text{cal}}{\text{mol} \cdot ^\circ\text{C}} + 2 \frac{\text{cal}}{\text{mol} \cdot ^\circ\text{C}} \right) (120^\circ\text{C}) \\ &= 30 \text{ kcal} \end{aligned}$$

**4B.** What is the internal energy change of the nitrogen sample?

$$\begin{aligned} \Delta U &= n(\bar{C}_V)\Delta T \\ &= \left( \frac{1000 \text{ gram}}{28 \text{ gr/mole}} \right) \left( 5 \frac{\text{cal}}{\text{mol} \cdot ^\circ\text{C}} \right) (120^\circ\text{C}) \\ &= 21.4 \text{ kcal} \end{aligned}$$

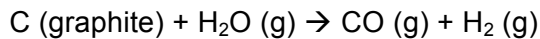
**4C.** How much work is done?

$$\begin{aligned} W &= \Delta U - q = n(\bar{C}_V)\Delta T \\ &= 21.4 \text{ kcal} - 30 \text{ kcal} \\ &= -8.6 \text{ kcal} \end{aligned}$$

8.6 kcal of work performed.

**Problem 5 (20 Points) Thermochemistry**

Consider the following reaction:



The standard enthalpy of reaction at  $T=298.15\text{K}$  is  $\Delta H_{T=298.15}^0 = 131.28 \frac{\text{kJ}}{\text{mol}}$ . What is the standard enthalpy of reaction at  $125^\circ\text{C}$ ? Assume constant molar heat capacities.

$$\Delta H_{\text{reaction}}^{\circ}(T = 398.15\text{K}) = \Delta H_{\text{reaction}}^{\circ}(T = 298.15\text{K}) + \int_{T=298.15\text{K}}^{T=398.15\text{K}} \Delta C_{P,\text{rxn}} dT$$

$$\Delta C_{P,\text{rxn}} = \sum_i \nu_i C_{P,i}^{\circ} = (1)(29.1 \frac{\text{J}}{\text{mol K}}) + (1)(28.8 \frac{\text{J}}{\text{mol K}}) - (1)(8.5 \frac{\text{J}}{\text{mol K}}) - (1)(33.6 \frac{\text{J}}{\text{mol K}})$$

$$\Delta C_{P,\text{rxn}} = 15.8 \frac{\text{J}}{\text{mol K}}$$

$$\Delta H_{\text{reaction}}^{\circ}(T = 398.15\text{K}) = 131.28 + \int_{T=298.15\text{K}}^{T=398.15\text{K}} \Delta C_{P,\text{rxn}} dT = 131.28 + \left(0.0158 \frac{\text{kJ}}{\text{mol K}}\right)(100\text{K}) = 132.86 \frac{\text{kJ}}{\text{mol}}$$



**Problem 6. Extra Credit (5 Points)** Show explicitly that the reversible work to accelerate a resting mass 'm' from zero initial velocity to final velocity 'v<sub>x</sub>' along the x-direction is ½ m v<sup>2</sup>. Specifically:

$$U_{KE} = \int dW = \frac{1}{2} m v_x^2$$

The response will require showing how the force on the mass, for which there is an explicit mathematical form, leads to the expression involving velocity.

**Solution:**

$$U_{KE} = \int dW$$

$$dW = F_x dx = m \left( \frac{dv_x}{dt} \right) dx$$

$$dx = v_x dt$$

$$dW = F_x dx = m \left( \frac{dv_x}{dt} \right) v_x dt$$

$$dW = F_x dx = m v_x dv_x$$

$$dW = d \left( \frac{1}{2} m v_x^2 \right)$$

$$\int dW = \int_0^{v_x} d \left( \frac{1}{2} m v_x^2 \right)$$

$$U_{KE} = \int dW = \frac{1}{2} m v_x^2 - 0 = \frac{1}{2} m v_x^2$$

## 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)

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