Chem132A Discussion 4 Homework

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1 Thermodynamics of Mixtures

When considering liquid mixtures it is important to realize that there is an associated vapour phase above the liquid (that is in equilibrium with the liquid phase). When we try to solve problems containing mixtures, we are usually making assumptions about how the liquid and the gas phases behave.

An **Ideal Solution** (aka ideal mixture) essentially assumes that the molar Enthalpy and molar Volume of Mixing are zero. Physically these assumptions imply that the interactions between all atom types are zero (A-A = B-B = A-B = 0). If this is true, than breaking a bond between A-A to form A-B will have no change in the energy of the system and subsequently the change in Enthalpy due to mixing must be 0 (Note: if the interactions were all equal but not 0, the enthalpy of mixing would still be 0, the Volume of Mixing may not be 0). Therefore, a mixture with a larger Enthalpy of mixing is 'less-ideal' than a mixture with a small Enthalpy of mixing.

Rault's law is obtained by setting the chemical potential of the liquid phase equal to the vapour phase and solving. Essentially it assumes that both the liquid and vapour phases are ideal (giving the simplest possible description of a mixture). Because the liquid and vapour phases are related people generally say a solution behaves ideally if it obeys Rault's Law.

If you want to consider a non-ideal system, you can assume either the gas, the liquid, or both phases are non-ideal. The **Activity Coefficient** is a parameter used to capture non-ideal behavior in liquids, the **Fugacity Coefficient** captures non-ideal behavior in gases.

1.1 Concepts

Does a large Henry's Law constant imply a gas is more or less soluble in a liquid (Defend your answer algebraically, and in words)?

1.2 Concepts Round Two

If we were to consider a **Non-Ideal** solution, we can have either positive or negative deviations from Rault's Law. Take the solution to be between molecules A and B (with equal amounts of each).

A positive deviation is described by same-type molecule interactions being stronger than mixed (A-A > A-B). In this scenario do you expect the molar volume to increase or decrease upon mixing? What would a negative deviation imply about the interactions, and what would happen to the molar volume upon mixing?

What about the vapour pressure for each case (will it be larger or smaller than predicted by Rault's Law)?

1.3 Derivation Time

Ideal (non-simple) solutions are generally defined as either

$$\mu_i - \mu_{\text{pure},i} = RT \ln x_i \tag{1}$$

Or as

$$f_i = x_i f_{\text{pure},i} \tag{2}$$

Show that both of these definitions are consistent (they are the same thing) when I define the fugacity to be:

$$RT \ln \frac{f_i}{f_i^0} = \mu_i - \mu_i^0 \tag{3}$$

(Note a superscript ^{0} implies a reference state of your choosing)

2   Ideal Mixture Calculations

Consider the mixing of two samples of different mono-atomic ideal gases at two different temperatures, T_H (Temperature Hot) and T_C (Temperature Cold). Initially, one mole of gas A at T_H is enclosed in the left side of a container with volume $\frac{V_a}{2}$. While one mole of gas B at T_C is enclosed in the right side, also with volume $\frac{V_a}{2}$. The system is separated from the surroundings by rigid adiabatic walls (q=0). The hatch separating the gases is opened and system is allowed to mix. After mixing the hatch is then closed.

For this problem define your system to be the entire box (not just a single side).

2.1   Calculating T_f

Calculate the final temperature in terms of T_H and T_C.

Hint : For an ideal monoatomic gas :

$$C_v = \frac{3R}{2} \tag{4}$$

Hint 2: This is an adiabatic process therefore q = 0 , this also an Ideal Gas meaning U(T), (both sides of the box have an associated temperature change, because heat cannot enter or leave the overall temperature change of the system is 0). This implies the work associated with the process is 0.

2.2   Entropy of Mixing

We know there is an associated entropy change with this process (you should be able to guess if it is positive or negative). Calculate the Entropy of Mixing associated with this process.

Hint: You will want to calculate the entropy associated with the temperature change, and the entropy change associated with the new conformations of the molecules after mixing.

3   van der Walls Phase Diagram

For the vdw Equation of State, a bunch of mathematics can be used to determine the critical temperature, pressure, and volume as

$$V_{m,c} = 3b, \qquad P_c = \frac{a}{27b^2}, \qquad T_c = \frac{8a}{27bR} \tag{5}$$

Consider Krypton as described by the vdw EOS. Compute the critical pressure, temperature, and molar volume for Krypton using the above expressions.

Once you have computed these values, make three separate isotherms (PV diagrams holding T constant) where you plot values above the critical temperature, below the critical temperature, and at the critical temperature.