

**Quiz 6**  
**CHEM 323**  
**Fall 2008**

Name: \_\_\_\_\_

1. (5 Points) A 5.00-liter vessel is divided into two equal parts by a removable partition. In one half of the vessel there is nitrogen at a pressure of 1.00 atm and at 25.0 °C, and in the other half is hydrogen at the same temperature and pressure. Calculate  $\Delta_{mix}G$  and  $\Delta_{mix}S$  when the partition is removed. Assume that the gases are ideal.

**To determine  $\Delta_{mix}G$  we use the equation  $\Delta_{mix}G = nRT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$ . The first step is to find the mole fraction of each gas.**

**Since the pressure, temperature and volume of each gas is the same (1.00 atm, 25.0 °C and 2.50 L, respectively), the number of moles of each gas must be the same**

**( $n_{N_2} = n_{H_2}$ ). And so we may write  $\chi_{N_2} = \chi_{H_2} = \frac{1}{2}$ .**

**Since the total number of moles,  $n$ , equals the sum of the number of moles of each gas and the gases are ideal, we may write  $\Delta_{mix}G = pV(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$ .**

**Substituting gives**

$$\Delta_{mix}G = pV \left( \frac{1}{2} \ln \left( \frac{1}{2} \right) + \frac{1}{2} \ln \left( \frac{1}{2} \right) \right) = pV \left( -\frac{1}{2} \ln 2 - \frac{1}{2} \ln 2 \right) = -pV \ln 2$$

$$\Delta_{mix}G = -(1.00 \text{ atm})(5.00 \text{ L})(\ln 2) \left( \frac{101.325 \text{ J}}{1 \text{ L} \cdot \text{atm}} \right) = -0.351 \text{ kJ}$$

**To find  $\Delta_{mix}S$ , we can either use the expression  $\Delta_{mix}S = -nR(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$ ,**

**integrate the expression  $\left( \frac{\partial G}{\partial T} \right)_p = -S$ , or realize that  $\Delta_{mix}S = -\frac{\Delta_{mix}G}{T}$  for ideal**

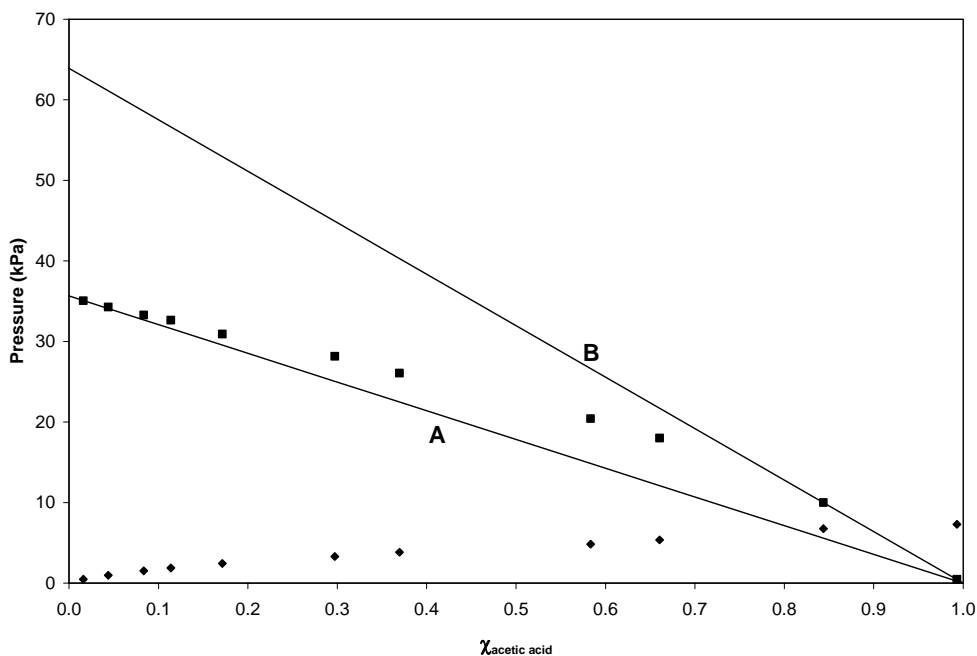
**mixtures ( $\Delta_{mix}H = 0$ ).**

$$\Delta_{mix}S = -\frac{\Delta_{mix}G}{T} = \frac{0.351 \times 10^3 \text{ J}}{298.15 \text{ K}} = +1.18 \text{ J} \cdot \text{K}^{-1}$$

**For this process  $\Delta_{mix}G$  is -0.351 kJ and  $\Delta_{mix}S$  is +1.18 J·K<sup>-1</sup>.**

2. A graph of the vapor pressure of benzene (■) and acetic acid (◆) above mixtures of the two compounds as a function of the mole fraction of acetic acid ( $\chi_{\text{acetic acid}}$ ) is shown below. The data at high and low benzene concentrations were fit to linear equations in the mole fraction of benzene ( $\chi_{\text{benzene}}$ ), as given in the table.

	Line A (—)	Line B (---)
Slope (kPa)	$35.7 \pm 0.2$	$63.9 \pm 0.2$
Intercept (kPa)	$0.0 \pm 0.2$	$0.01 \pm 0.01$



a. (5 Points) What is the vapor pressure of pure benzene?

The vapor pressure of pure benzene may be obtained from Raoult's Law when benzene is the solvent ( $\chi_{\text{acetic acid}}$  is small), which is on the left side of the above diagram and is described by line A. The vapor pressure will be the value of the pressure when  $\chi_{\text{benzene}} = 1$  ( $\chi_{\text{acetic acid}} = 0$ ). Substituting this into equation A yields

$$p = 35.7(1.00)\text{kPa} + 0.0\text{kPa} = 35.7\text{kPa}$$

Thus, the vapor pressure of pure benzene is 35.7 kPa.

b. (5 Points) What is the Henry's Law constant of benzene in acetic acid?

This is obtained from a fit of the vapor pressure when benzene is the solute ( $\chi_{\text{acetic acid}}$  is large), which is the right side of the figure and is described by line B. To obtain the Henry's Law constant, we extrapolate this line back to  $\chi_{\text{benzene}} = 1$ . Substituting this value into the equation for line B gives

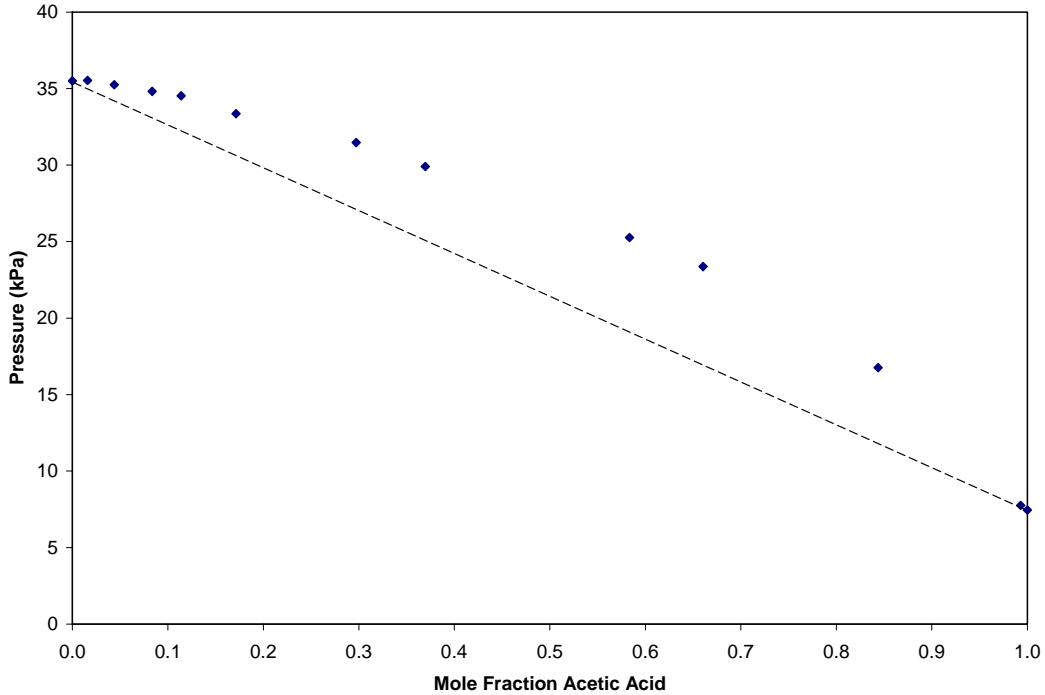
$$p = 63.9(1.00)\text{kPa} + 0.01\text{kPa} = 63.9\text{kPa}$$

The Henry's Law constant for benzene in acetic acid is 63.9 kPa.

c. (2 Points) Which is more volatile, benzene or acetic acid? Why?

**The vapor pressure of benzene is obtained when  $\chi_{\text{acetic acid}} = 0$  and the vapor pressure of acetic acid may be obtained when  $\chi_{\text{acetic acid}} = 1$ . From inspection of the diagram, it is clear that the vapor pressure of benzene is higher than that of acetic acid, which means that it is easier to boil benzene than acetic acid and so benzene is more volatile.**

d. (2 Points) Shown below is the graph of the total pressure in the benzene-acetic acid system as a function of the mole fraction of acetic acid. Draw in a line showing what the total pressure would be if Raoult's Law were followed at all compositions.



e. (4 Points) What is the sign on  $G^E$  for this system? Explain how you know this and what it means for the intermolecular interactions occurring in the mixture.

**$G^E$  is positive because there is a positive deviation from Raoult's Law, that is to say the observed vapor pressure of the mixture is higher than expected based on the mole fraction. This means that it is energetically more favorable for benzene and acetic acid to leave the liquid mixture and enter the gas phase. Assuming that the mixture forms a regular solution ( $S^E = 0$ ), then this is the result of a positive  $H^E$ , which indicates that repulsive intermolecular interactions between the acetic acid and benzene are important in this system.**

*Note that this makes sense in that benzene is nonpolar and acetic acid is polar. The only attractive interactions between their molecules are van der Waals forces, which are weak at best. Thus, repulsive interactions (such as the molecules getting too close to each other) can dominate.*