

CH353 – Physical Chemistry I
Spring 2013, Unique 52575

Exam 4 – April 5, 2013

Name: Key

Always assume ideal gas unless directed otherwise.

You may use any material that does not have a heartbeat and does not connect to the internet or cellular network.

Honor Code:

“The core values of the University of Texas at Austin are learning, discovery, freedom, leadership, individual opportunity, and responsibility. Each member of the University is expected to uphold these values through integrity, honesty, trust, fairness, and respect toward peers and community.”

I certify that the work on this exam is entirely my own.

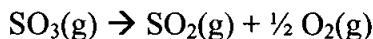
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1. (20 points) Determine if the following statements are true or false.

- a. True False In a two-component solution, if one component obeys Raoult's law everywhere, the other component must obey Henry's law everywhere also.
- b. True False For a given composition of any chemical reaction, if $Q > K_P$, the reaction will be pushed towards the products.
- c. True False For an endothermic reaction, K_P decreases as P_{tot} decreases.
- d. True False For an endothermic reaction, K_P decreases as T decreases.
- e. True False If $\ln K_P$ of a reaction is plotted as a function of the inverse of the temperature at which the reaction occurs (i.e. a plot of $\ln K_P$ versus $1/T$), if the slope of the curve is positive then the reaction is exothermic.
- f. True False Energy is quantized.

2. (15 points) In class, we examined the decomposition of $\text{SO}_3(\text{g})$:



and found that $K_P = 2.0 \times 10^{-4}$ and $z_{eq} = \left(\frac{\sqrt{2} K_P}{P_{tot}^{1/2}} \right)^{2/3}$. At what pressure will the $\text{SO}_3(\text{g})$

completely decompose, assuming that you start with n moles of $\text{SO}_3(\text{g})$ and none of the products?

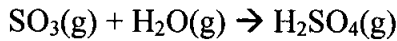
i.e. what is P_{tot} at $z_{eq} = 1$?

$$z_{eq} = \left(\frac{\sqrt{2} K_P}{P_{tot}^{1/2}} \right)^{2/3}; \quad z_{eq}^{3/2} = \frac{\sqrt{2} K_P}{\sqrt{P_{tot}}}$$
$$P_{tot} = \left(\frac{\sqrt{2} K_P}{z_{eq}^{3/2}} \right)^2 = \left(\frac{\sqrt{2} (2.0 \times 10^{-4})}{1^{3/2}} \right)^2$$

$$P_{tot} = 8.0 \times 10^{-8} \text{ bar}$$

this pressure is low, but it is easily achievable by standard laboratory equipment.

3. (30 points) $\text{SO}_3(\text{g})$ can react with $\text{H}_2\text{O}(\text{g})$ in air to form sulfuric acid:



The following information may be useful.

species	ΔH_f° (kJ/mol)	S_m° (J/K mol)	ΔG_f° (kJ/mol)
$\text{O}_2(\text{g})$	0	205.1	0
$\text{H}_2\text{O}(\text{g})$	-241.8	188.7	-228.57
$\text{SO}_2(\text{g})$	-296.9	248.2	-300.2
$\text{SO}_3(\text{g})$	-395.7	256.8	-371.1
$\text{H}_2\text{SO}_4(\text{g})$	-814.0	156.9	-690.0

a) Determine the ratio of H_2SO_4 to SO_3 at equilibrium if this reaction is carried out in the open atmosphere of 1 bar and 298 K, where the partial pressure of water vapor is constant at 0.031 bar and there are initially n moles of $\text{SO}_3(\text{g})$. i.e. $P(\text{H}_2\text{O}) = 0.031$

$$\Delta G_{rxn}^\circ = \Delta G_f^\circ(\text{H}_2\text{SO}_4) - \Delta G_f^\circ(\text{H}_2\text{O}) - \Delta G_f^\circ(\text{SO}_3) = -90.3 \text{ kJ/mol}$$

$$K_p = \exp\left[\frac{-\Delta G_{rxn}^\circ}{RT}\right] = 6.7 \times 10^{15} \gg 1$$

$$K_p = \frac{P(\text{H}_2\text{SO}_4)}{P(\text{SO}_3)P(\text{H}_2\text{O})} \quad ; \quad \frac{P(\text{H}_2\text{SO}_4)}{P(\text{SO}_3)} = K_p(P(\text{H}_2\text{O})) = (6.7 \times 10^{15})(0.031)$$

$$\frac{P(\text{H}_2\text{SO}_4)}{P(\text{SO}_3)} = 2.1 \times 10^{14}$$

b) $\text{SO}_3(\text{g})$ is a common byproduct of many industrial processes, and is the principal source of the acid in acid rain. Describe, with as much quantitative detail as necessary, how your answer to part a) will change at altitudes where both atmospheric pressure and temperature are significantly lower than the conditions given in part a). You may assume that the fraction of the atmosphere composed of water vapor remains the same as in part a).

$$\text{As } T \downarrow, \quad K_p(T_2) = K_p(T_1) \exp\left[\frac{-\Delta H_{rxn}^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

$$\Delta H_{rxn}^\circ = \sum \nu_c \Delta H_{f,c}^\circ = -178 \text{ kJ/mol} \quad (\text{i.e. exothermic})$$

So we expect $K_p(T_2) > K_p(T_1)$

$$K_p(T_2) = (6.7 \times 10^{15}) \exp\left[\frac{-(-178 \times 10^3 \text{ J/mol})}{8.314 \text{ J/Kmol}} \left(\frac{1}{200 \text{ K}} - \frac{1}{298 \text{ K}}\right)\right]$$

$$K_p(T_2) = 1.3 \times 10^{31}$$

!! large

over \rightarrow

as $P \downarrow$, $k_p = k_x P_{\text{TOT}}^{\sum \nu_L} = k_x P_{\text{TOT}}^{1-1-1} = k_x P_{\text{TOT}}^{-1}$

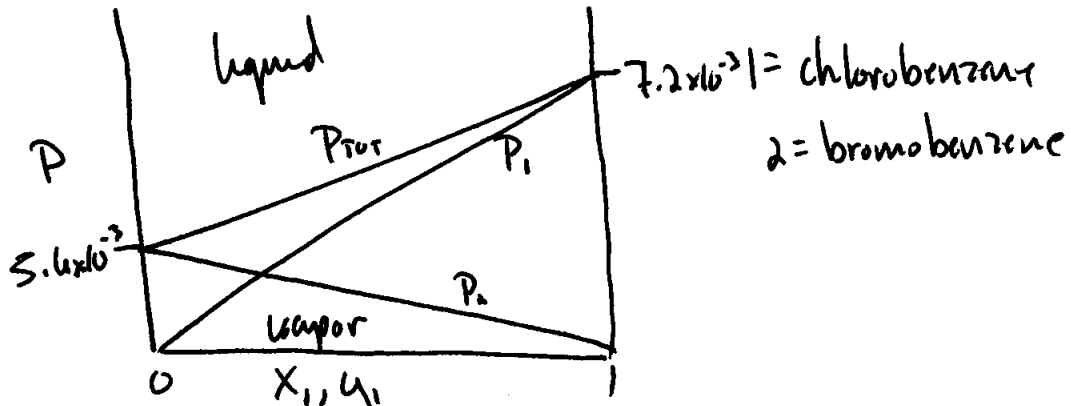
Since k_p remains constant (at $\Delta T = 0$), as P_{TOT} decreases by a factor of 10, (i.e. $P_{\text{TOT}} = 0.1 \text{ bar}$), P_{TOT}^{-1} increases by a factor of 10 (i.e. $P_{\text{TOT}}^{-1} = 10 \text{ bar}$), so k_x will have to decrease by a factor of 10 to compensate (i.e. k_x at $P_{\text{TOT}} = 0.1 \text{ bar} = 0.1 (k_x \text{ at } P_{\text{TOT}} = 1 \text{ bar})$).

The effects of lowering T and P are thus in opposite directions, but the effect of temperature will be substantially larger than the effect of pressure (because of the exponent).

4. (25 points) Chlorobenzene and bromobenzene form an ideal solution when mixed at room temperature. The following data may be useful:

Species	T_{vap} (K)	P^* (bar)
C_6H_5Cl	404	7.2×10^{-3}
C_6H_5Br	429	5.6×10^{-3}
C_6H_5OH	455	4.2×10^{-3}

a) Draw a pressure composition diagram of this ideal solution, carefully labeling all axes.



b) A solution was made that contained 25% chlorobenzene. Determine the mole fraction of both species in the liquid and vapor phases.

$$X_1 = 0.25 \Rightarrow X_2 = 0.75$$

$$P_{TOT} = P_1 + P_2 = X_1 P_1^* + X_2 P_2^* = (0.25)(7.2 \times 10^{-3}) + (0.75)(5.6 \times 10^{-3})$$

$$P_{TOT} = 0.006 \text{ bar}$$

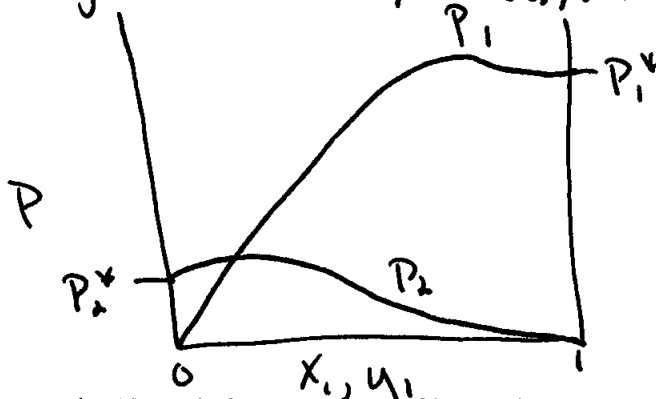
$$y_1 = \frac{P_1}{P_{TOT}} = \frac{(0.25)(7.2 \times 10^{-3})}{0.006} = 0.30 = y_1$$

$$y_2 = 0.70 = y_2$$

So the vapour is enriched in the more volatile species as expected

c) When bromobenzene and phenol (C_6H_5OH) are mixed, they do not form an ideal solution. Draw a pressure composition diagram of this solution, carefully labeling all axes.

Phenol cannot only make H-bonds, so we expect repulsive interactions



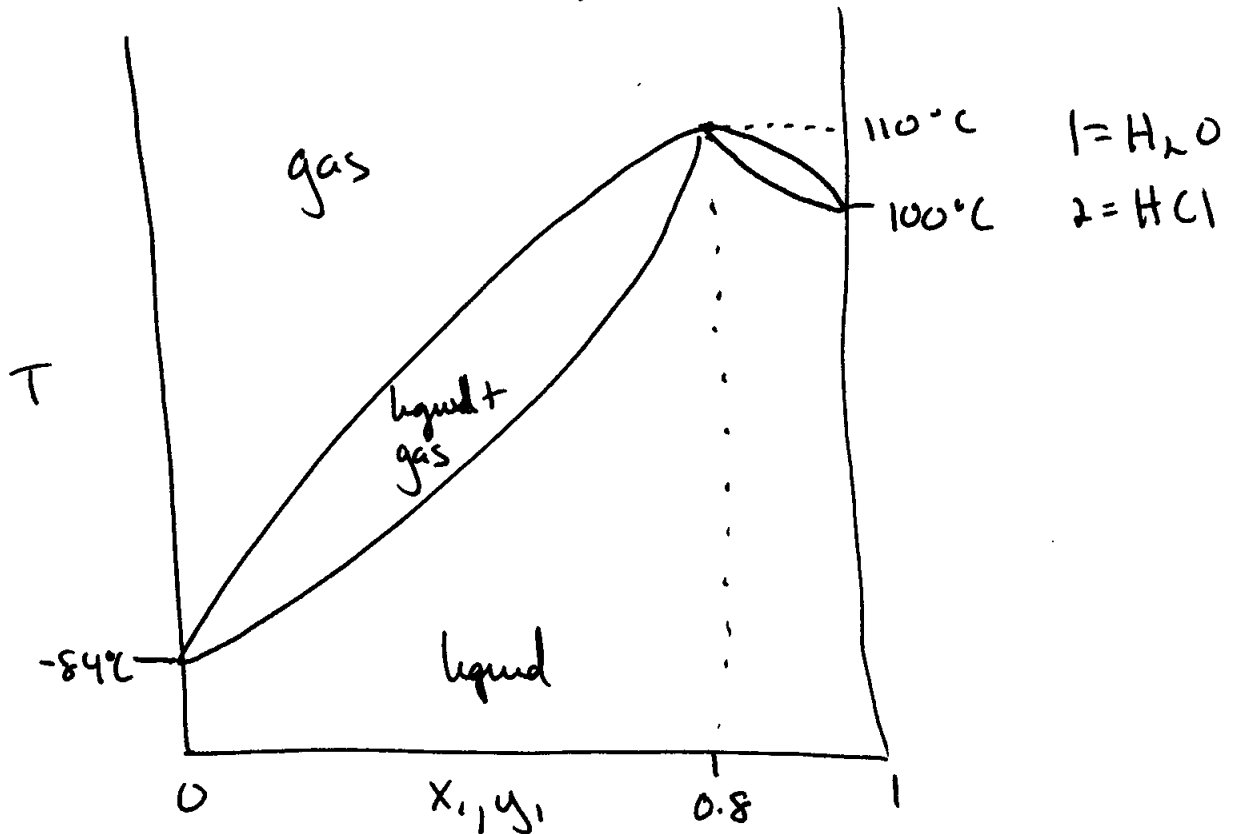
In both cases we expect repulsive Henry's law behavior until the endpoints.

d) Do you expect the Henry's law constant of bromobenzene and phenol in this solution to be higher or lower than their respective P^* ? Justify your answer.

Because we have repulsive interactions, $k_H > P^*$ for both species

5. (10 points) Azeotropes are nonideal solutions that we have not discussed in class. Azeotropes occur when a particular composition of a solution has either a higher or lower boiling point compared to the two pure components. One example of an azeotrope is a solution of hydrochloric acid. Pure hydrogen chloride boils at -84°C and pure water boils at 100°C , but in a composition of 80% by ~~weight~~^{mole} H_2O , the solution boils at 110°C .

a) Using this information, draw a temperature composition diagram of a solution of hydrogen chloride in water. Carefully label all axes and be sure the phase and composition of each region are clear. You may not assume that this solution obeys Raoult's law.



b) Provide a physical explanation for why this solution might show this behavior.

When HCl dissolves in H_2O it completely dissociates into $\text{H}^+ + \text{Cl}^-$. These two ions both can associate strongly with H_2O , both by H-bond accepting (Cl^-) and donating (H^+) and by Coulombic interactions between the charged ions and the molecular dipole of water. At $x_1 = 0.8$, this composition maximizes all attractive intermolecular forces and it gives the solution a lower vapor pressure (higher T_{vap}) than either of the two pure components.