

INDIVIDUAL

INDIVIDUAL EXAM

WUCT 2018

60 minutes are allotted for the individual round. Questions on the individual exam will consist of multiple parts that must each be answered with numerical results or short answers. Only answers written in the given space, or clearly labelled answers on the back of the page, will be graded. Correct answers with reasonable supporting work will receive full credit, while correct answers without work will not receive full credit. If more than one answer is given when only one answer is asked for on the question, that question will be marked as completely incorrect. While team members may be placed together in the same exam room, they are not permitted to communicate with other team members or their coach in any way during the individual rounds. No electronics of any kind can be used during the exam, except for a non-programmable scientific calculator. Cell phones must be turned off, and watches must be removed. The time will be projected and/or announced in the exam rooms. Necessary equations, constants, and a periodic table will be provided. Cheating will NOT be tolerated.

Student 1 ID			
0	0	0	0
1	1	1	1
2	2	2	2
3	3	3	3
4	4	4	4
5	5	5	5
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Team: _____

Team ID: _____

Student 1: _____

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INDIVIDUAL

Question 1

This question is designed to test your knowledge of acid/base chemistry as well as acid/base laboratory techniques.

- a. (2 points) Daniel just gave you a mystery solution of some unknown concentration of HCl. You tried determining the concentration of the solution with pH paper but you ended up burning the paper. Daniel knows the concentration, and he gives you a hint that it's 2^x M, where x is an integer. You have some materials to help you. You have an excess of deionized water and as much pH paper as needed. Daniel also tells you that the pH paper turns a characteristic dark red when the pH is 0.903. Explain how you would go about finding the concentration of the original solution. Assume you can accurately identify that characteristic dark red color.

Dark red color is noticed at 0.903 M $\Rightarrow [H^+] = 0.125 = 2^{-4}$ Because the pH paper was burned, x is greater than 0. Keep diluting the solution by a factor of 2, testing each time until the dark red color is seen. Then work backwards and you can find the actual concentration.

- b. (3 points) How many mL of a 0.500M NaOH solution would you have to add to a 50.0 mL of a 0.300M acetic acid solution to create the strongest possible buffer? What will the pH be of that buffer (the K_a of acetic acid is 1.8×10^{-5})? What will the pH be after adding 10.0 more mL of the NaOH solution?

The strongest possible buffer is created when moles of acetate = moles of acetic acid. The number of moles of acetic acid originally = $0.050 \text{ L} * 0.300 \text{ M} = 0.015$ moles. Because NaOH and acetic acid react in a 1:1 ratio to form 1 mole of acetate, $0.015/2$ or 0.0075 moles of NaOH must be added.

$1000 * (0.0075 \text{ mol} / 0.500 \text{ M}) = 15 \text{ mL}$. $K_a = 1.8 \times 10^{-5} \Rightarrow pK_a = 4.74$. $pH = pK_a$ at the strongest point, so $pH = 4.74$.

After adding 10 mL NaOH, $0.010 \text{ L} * 0.500 \text{ M} = 0.005$ moles of NaOH are added. Using Henderson Hasselbach, $pH = 4.74 + \log (0.0125/0.0025) = 5.44$.

- c. (5 points) If you titrate that acetic acid solution with that NaOH solution, what volume of NaOH is needed to reach the equivalence point, and what will the pH be at that equivalence point?

The equivalence point will be reached at $15 \text{ mL} * 2 = 30 \text{ mL}$ of NaOH added. At that point 0.015 mol of acetate will be in 80 mL of solution $\Rightarrow [\text{acetate}] = 0.1875 \text{ M}$. Using the K_b eq where $K_b = x^2 / (0.1875 - x)$, $x = 1.02 \times 10^{-5} = [OH^-]$. pOH is therefore 4.99, making the pH 9.01.

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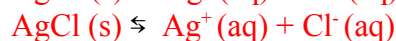
Question 2

This question is designed to test your knowledge of solubility and separations. For all questions, assume no volume change upon addition. Jerry just gave you a solution containing 0.1M of Cl^- ions and 0.2M of Br^- ions. He tasks you with separating the two (meaning that you are only removing one ion *out of solution*, not both at the same time). The only material he gives you is some Ag^+ . The solubility constant of AgBr is $4.1 \times 10^{-13} \text{M}$ and that the solubility constant of AgCl is $1.7 \times 10^{-10} \text{M}$

- a. (2 points) Why would Ag^+ be useful?

AgCl and AgBr are both insoluble and have K_{sp} 's that differ by 3 orders of magnitude. This means that one ion can precipitate out of solution while the other remains in solution.

- b. (2 points) Write out the two equilibria seen in the solution if silver is added to the solution.



- c. (4 points) How much silver would have to be added for a precipitate to be noticed?
Which ion precipitates out and at what concentration of Ag^+ ?

Q must be greater than or equal to K_{sp} for precipitation to occur. For Bromide, the concentration of silver ion at which precipitation will occur is $K_{\text{sp}} / [\text{Br}^-] = 2.1 \times 10^{-12} \text{M}$. Similar calculation for Cl^- yields $1.7 \times 10^{-9} \text{M}$. Therefore, Bromide will precipitate out first.

- d. (2 points) You continue adding silver and notice that the concentration of silver increases while the concentration of the other ion that you determined in part c decreases. This seems obvious, but why is this necessary in terms of K_{sp} ?

As Br^- leaves solution, Ag^+ must increase in concentration/be continuously added to keep Q greater than or equal to K_{sp} .

- e. (2 points) When should you stop adding Ag^+ ? In other words, when would the separation essentially end?

The separation would end when $[\text{Ag}^+] = 1.7 \times 10^{-9} \text{M}$. At that point, both ions will precipitate out, ending the separation.

- f. (3 points) Calculate how much of the first ion is left in the solution after the separation.

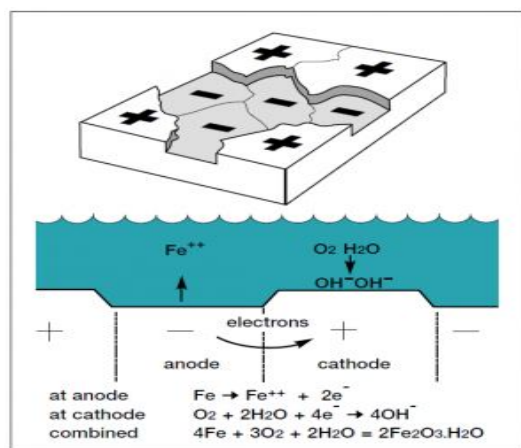
Using the K_{sp} equation, $[\text{Br}^-] = K_{\text{sp}} / [\text{Ag}^+] = 2.41 \times 10^{-4} \text{M}$

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Question 3

This question is designed to test your knowledge of oxidation-reduction reactions. In shipbuilding, the main material used to build a ship is steel. However, corrosion of the steel can occur, presenting many problems for shipbuilders. The main process of corrosion is galvanic corrosion. Galvanic corrosion occurs when two different metals have physical or electrical contact with each other and are immersed in a common electrolyte. In a galvanic couple, the more active metal (the anode) corrodes at an accelerated rate and the more noble metal (the cathode) corrodes at a slower rate. It is very easy for microscopic areas of the exposed steel to become relatively anodic or cathodic to one another. As you can see from the diagram below, a large number of such areas can develop in a small section of the exposed steel. In the presence of oxygen and wet air, galvanic corrosion first converts Fe (s) into Fe(OH)₂ (aq), which is easily further oxidized by O₂ (g) to form Fe₂O₃ (s), the main component of rust.



- a. (4 points) Write down the net ionic formula of the formation of Fe(OH)₂ (aq) and the net ionic formula of further oxidation of Fe(OH)₂ (aq).

Oxidation: $\text{Fe (s)} \rightarrow \text{Fe}^{2+} + 2\text{e}^{-}$. Fe^{2+} further reacts with OH^{-} to form Fe(OH)₂. Reduction: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \rightarrow 4\text{OH}^{-}$. Further oxidation: $4\text{Fe(OH)}_2 + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 4\text{H}_2\text{O}$

- b. (3 points) Steel is not pure iron. Instead, it is the alloy of iron and Cu, Al, Mn, or C in order to improve the solidity, density, etc. How do these impurities affect the corrosion rate of steel and why?

Metals like Cu and Al are more easily reduced than Fe, and function as cathodes, forcing Fe to be the anode where it gets oxidized. This speeds up rust formation.

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- c. (3 points) Compared to ships in freshwater river or lake, ocean liners corrode faster. Why?

Dissolved salts in the saltwater provide a salt bridge, favoring galvanic corrosion.

- d. (5 points) To prevent corrosion, a ship company is using a method called sacrificial anodic protection. In this method, the shipbuilders put a layer of coating of another metal onto the ship body. These metal slices will act as the anode, thus being corroded first. Since the main body of ship is acting as cathode, the corrosion rate of steel will be much slower. Given that:

Reaction	Electrochemical Potential (E°)
$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.76
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.44
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.34

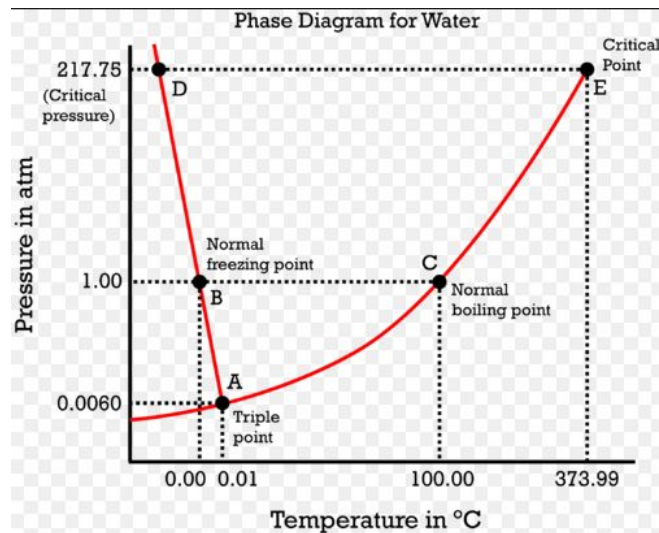
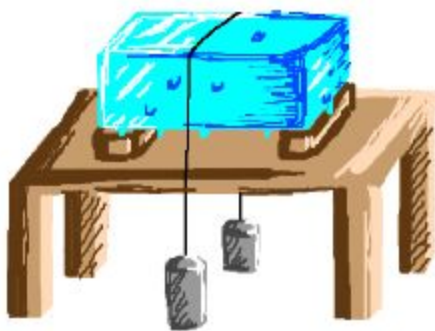
Which metal, Zn or Cu, could be used as sacrificial anode? Why?

Zn since it is more likely to get oxidized compared to Fe.

INDIVIDUAL

Question 4

(5 points) This question is designed to test your knowledge of phase changes and its dependencies on pressure and temperature. Professor X started off class on Monday by presenting you with the apparatus shown below. Professor X bets you \$5 that the wire will cut through the ice by the end of the class period, and the ice will be a whole single block. Do you take the bet? Assume you are in a freezing classroom at $0\text{ }^{\circ}\text{C}$. Explain your choice using this phase diagram for water.



Do not take the bet. Water is anomalous in that when pressure increases, the melting point actually decreases. As the wire applies pressure to that region of ice, the ice will melt because the melting point of ice in that region will decrease slightly. As the wire moves through that region, the pressure will be relieved, and the melting point will return to normal, re-freezing the water. The same process will happen again for the next bit of ice until the wire has made it through the entire block. In the end, the block will be in one piece.

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Question 5

This question is designed to test your knowledge of gas laws.

- a. (5 points) Using Raoult's and Dalton's laws, what is the composition of ethanol in the vapor produced by a 60/40 molar mixture of ethanol/water at 25 °C. The vapor pressure of water at this temperature is 0.0313 atm, and the vapor pressure of ethanol is 0.08 atm.

$P_T = P_{\text{ethanol}} + P_{\text{Water}}$ and $P_{\text{ethanol}} = (\text{mole fraction of ethanol}) * (\text{Vapor pressure of pure ethanol})$.
The same goes for water.

So, $P_{\text{ethanol}} = 0.60 * 0.08 \text{ atm} = 0.048 \text{ atm}$, and similar calculation with water yields a P_{water} of 0.01252 atm.

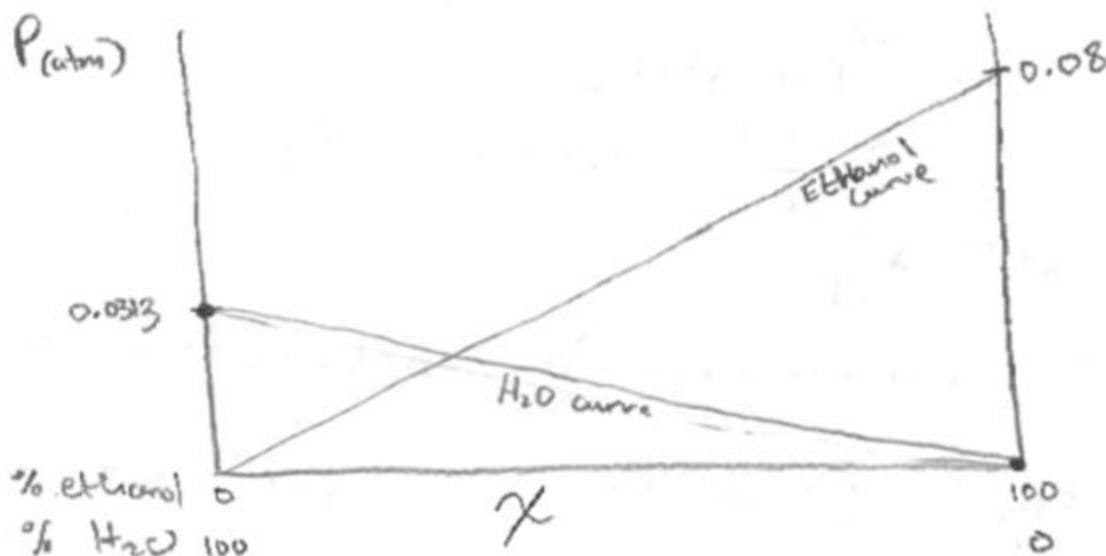
Using the first equation, percentage composition of ethanol = $(P_{\text{ethanol}}/P_{\text{Total}}) * 100\% = 79.3\%$ ethanol.

Subtraction from a 100% gives you 20.7% Water.

- b. (3 points) If the size of the container is doubled, what happens to the vapor pressure?
What happens to the total number of moles in the vapor phase?

Vapor pressure will remain constant as it only varies with temperature but the number of moles of gas will have to double.

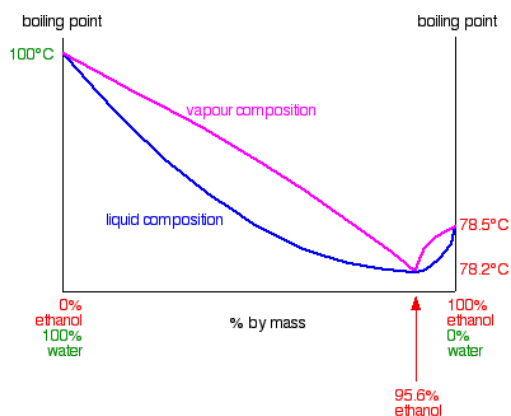
- c. (7 points) Using Raoult's Law, draw the pressure vs. mole fraction curve for ethanol in an ethanol water mixture. Do the same for water. What happens to total pressure as the composition percentage of ethanol increases?



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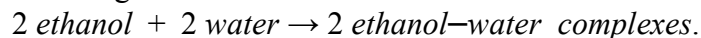
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- d. (2 points) Can you boil off pure ethanol given this curve starting with a 50/50 mixture of ethanol and water by mass? Explain.



Starting with a 50/50 mixture, repeated cycles of heating and cooling of the vapor will result in a 95% ethanol azeotrope. At that point, heating the liquid and condensing the vapor will not change the concentration.

- e. (3 points) It turns out that this type of boiling curve is formed because the ethanol-water interactions are weaker than the ethanol-ethanol interactions. Given this information, would mixing ethanol with water result in an endothermic reaction or exothermic reaction? Explain using this skeletal formula.



The reaction would be endothermic. Two strong ethanol-ethanol interactions and 2 strong Water-Water interactions are broken to form two weaker ethanol-water interactions. The heat released from bond formation is less than the heat inputted for bond breaking.

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INDIVIDUAL

Question 6

This question is designed to test your knowledge of ideal gases. Hydrogen peroxide (H_2O_2) is a mild antiseptic used for treating infections, scrapes, and burns (it's also used to make rocket fuel, but that's irrelevant to this problem).

- a. (2 points) If 3g of hydrogen peroxide is required to treat a scrape that a WUCT member sustained while handling a glass disposal box, how many moles of the compound are required? Assume no decomposition upon vaporization.

Molar mass of hydrogen peroxide is 34.014 g/mol. For 3g of hydrogen peroxide, $3\text{g}/34.014\text{ g/mol} = 0.0882\text{ mol}$ required

- b. Ideal gases are theoretical, and are only suitable approximations for a handful of gases such as H_2 and O_2 due to special properties.
- i. (2 points) Give one reason as to why hydrogen peroxide should not be considered an ideal gas, using the bonding structure of hydrogen peroxide. Assume that no decomposition occurs in the formation of hydrogen peroxide.

Hydrogen bonds can form between molecules, making collisions inelastic and not ideal.

- ii. (4 points) Assuming that hydrogen peroxide IS an ideal gas, express the pressure of the gas as a function of temperature (in Kelvin) for a sample of 0.084 moles of hydrogen peroxide in a container of volume 0.23 L.

$PV = nRT$, so $P = nRT/V$. Using 0.08206 for R yields $0.030T$.

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- c. As the constants a and b approach 0 in the van der Waals equation, it becomes the ideal gas law equation that you are familiar with. The constant a is a correction for the presence of intermolecular forces and the constant b is a correction for molecular size. Measures of pressure, volume, amount, and temperature of hydrogen peroxide are provided in the table below. (For this problem, assume hydrogen peroxide is always in its gaseous state.)

$$\left[P + a \left(\frac{n}{V} \right)^2 \right] \left(\frac{V}{n} - b \right) = RT$$

	P	V	n	T	a
Sample	104,610 Pa	0.0237 m ³	0.039 mol	311 K	3.67 J · mol · m ⁻³

- i. (4 points) Using the data presented in the table, obtain the value of the constant for hydrogen peroxide to an accuracy of at least 2 significant figures.

Solving for b and using 8.314 for R should yield 0.583 m³/mol.

- ii. (3 points) Comparing these constants a and b for hydrogen peroxide to HCL where $a = 3.67$ and $b = 0.0408$, is HCl or H₂O₂ more of an ideal gas? Why does this make sense?

HCl is more ideal. It has a smaller b value, meaning that it is smaller in size. It takes up less space, and is therefore more ideal.

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Question 7

This question is designed to test your knowledge of reactions at equilibrium using the Haber process. The Haber process was a crucial process developed in World War I by German Chemist Fritz Haber. The process allows for the mass production of Ammonia, a molecule crucial for crop growth.



The standard enthalpy change of the reaction is $-93 \text{ kJ} \cdot \text{mol}^{-1}$ and the standard entropy change of the reaction is $-198 \frac{\text{J}}{\text{mol} \cdot \text{K}}$. Assume these do not change with temperature.

- a. (2 points) Explain why the entropy change is negative

The entropy change is negative because 4 moles of gas are forming 2 moles of gas, reducing the degree of disorder in the system.

- b. (5 points) Calculate the equilibrium constant of the reaction at 298 K and standard conditions. Is this K_p or K_c ?

Using $dG = dH - TdS$, $dG = -34.0 \text{ KJ/mol}$. $dG = -RT \ln K_p$ at standard conditions. Solving for K_p yields $9.1E5$.

- c. (7 points) If 0.5 atm of N_2 and 1.5 atm of H_2 are placed in a rigid 1 liter container at room temperature (25 degrees Celsius), what are the equilibrium concentrations of each substance in the container? (Hint: Push the reaction one way and then use successive approximations)

	c) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$		
I	0.5	1.5	0
C	-0.5	-1.5	+1.0
I	0	0	1.0
C	+x	+3x	-2x
E	x	3x	1-2x

$$K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}}$$

$$K_p = \frac{(1-2x)^2}{(3x)^3(x)} = 9.1 \times 10^5$$

$$(1-2x)^2 = (2.46 \times 10^7) x^4 \text{ solve for } x$$

$$x = 1.42 \times 10^{-2} \text{ atm}$$

question asks for equilibrium pressures

$P_{\text{N}_2} = 1.42 \times 10^{-2} \text{ atm}$

$P_{\text{H}_2} = 4.26 \times 10^{-2} \text{ atm}$

$P_{\text{NH}_3} = 0.972 \text{ atm}$

equilibrium concentrations

$PV = nRT$

$\frac{P}{V} = C = \frac{n}{V} = \frac{P}{RT}$

$[\text{N}_2] = \frac{1.42 \times 10^{-2} \text{ atm}}{(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(298\text{K})} = 5.81 \times 10^{-4} \text{ M}$

$[\text{H}_2] = \frac{4.26 \times 10^{-2} \text{ atm}}{(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(298\text{K})} = 1.74 \times 10^{-3} \text{ M}$

$[\text{NH}_3] = \frac{0.972 \text{ atm}}{(0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}})(298\text{K})} = 3.97 \times 10^{-2} \text{ M}$

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- d. (2 points) After allowing the reaction to equilibrate, more H_2 is added to the reaction flask. What happens to the amount of N_2 in the flask?

$K_p = (P_{\text{Ammonia}})^2 / ((P_{H_2})^3(P_{N_2}))$. Therefore, if the partial pressure of H_2 increases, then $Q < K_p$ and the partial pressure of ammonia must increase to compensate. This means that more N_2 is consumed, resulting in less of it in the flask.

- e. (2 points) After allowing the reaction to equilibrate, a significant amount of some inert solid is added into the flask. Assuming no volume change, which way will the equilibrium shift? How will this change if there is a volume change?

If the volume does not change, nothing happens. If the volume does change, it will decrease, making $Q < K_p$, resulting in an equilibrium shift right.

- f. (2 points) If the temperature in the equilibrated flask is doubled (raised to 596K), which way will the equilibrium shift? (Hint: Use the Arrhenius equation or Le Chatelier's principle)

The Arrhenius equation shows that if we double the temperature, K_p will change significantly. Using $dG = dH - TdS$, $dG = 25.0 \text{ KJ/mol}$ at 596 K. Plugging this value and 596 K into the Arrhenius equation and dividing by the K_p found earlier shows that K_p is reduced by around 9 orders of magnitude when the temperature is double. Doubling the temperature also doubles the partial pressures of each gas in the flask, making $Q = 0.25 K_p$ at 298K. While Q is reduced, at 596 K, it will still be significantly larger than K_p at that temperature, yielding a shift left.