Put the first three letters of your LASTNAME in the boxes

EXAM 2 Free Response
Name:______________________
Sparks
EID:______________________
CH302 Spring 2014
Version Number:__________________

Answers must appear on this paper in the space provided. You should show your work.

1. For the reaction

\[ 2\text{COF}_2(g) \rightleftharpoons \text{CO}_2(g) + \text{CF}_4(g) \quad K_c = 2.00 \text{ at } 1000^\circ C \]

A. You initially have a 1L container into which you place 0.3 moles of \( \text{COF}_2 \), 0.2 moles of \( \text{CO}_2 \), and 0.2 moles of \( \text{CF}_4 \). Complete the following RICE table to show the change in concentrations and the concentrations at equilibrium in terms of an unknown variable “x”. (3 points)

<table>
<thead>
<tr>
<th></th>
<th>0.3M</th>
<th>0.2M</th>
<th>0.2M</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>-2x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.3-2x</td>
<td>0.2 + x</td>
<td>0.2 + x</td>
</tr>
</tbody>
</table>

**Total of 3 points: 1 point for each correct value in the equilibrium box.**

B. Set up the equilibrium expression you would need to solve to find the concentrations at equilibrium (3 points)

\[ K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2} \]

**Total of 3 points: 2 points for the correct position of products and reactants. 1 point for squaring \( \text{COF}_2 \) concentration. If the numerical/algebraic values from the RICE table were correctly filled in then full credit was awarded.**

C. Calculate \( Q \) and indicate which direction the reaction will proceed as it moves towards equilibrium (2 points)

\[ Q = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2} = \frac{[0.2M][0.2M]}{[0.3M]^2} = 0.44 \]

\( Q < K_c \) so the reaction will proceed to the right, toward the products.

**Total of 2 points: 1 point for correct \( Q \) value. 1 point for correct direction reaction proceeds.**

D. What is the concentration of \( \text{COF}_2 \) at equilibrium? (4 points)

\[ K_c = \frac{[\text{CO}_2][\text{CF}_4]}{[\text{COF}_2]^2} = \frac{(0.2 + x)(0.2 + x)}{(0.3 - 2x)^2} = \left(\frac{0.2 + x}{0.3 - 2x}\right)^2 = 2.00 \]

\[ \sqrt{2.00} \approx 1.414 = \frac{(0.2 + x)^2}{(0.3 - 2x)^2} = \frac{(0.2 + x)}{(0.3 - 2x)} \]

\[ 0.424 - 2.828x = 0.2 + x \]

\[ 0.224 = 3.828x \]

\[ 0.0585 = x \]

\[ [\text{COF}_2] = (0.3 - 2x) = 0.3 - 2(0.0585) \approx 0.183M \]

BE SURE TO COMPLETE BOTH THE FRONT AND BACK
Total of 4 points: 4 points for correct answer. If partial credit given: 1 point for the correct set-up/process. 1 point for getting correct x value. 2 points for correct answer. Any incorrect work from the RICE table or set-up of the K expression were considered and incorporated in each student's solutions.

E. How could you shift the equilibrium to generate more CF₄ by adding or removing material from the equilibrium mixture? Explain why this would shift equilibrium in this way. (2 points)

By adding more COF₂ or removing CO₂, the equilibrium will shift to the products (right side) and generate more products to reestablish equilibrium.

Total of 2 points: 1 point for stating a correct shift. 1 point for valid explanation.

F. Is there any other means besides adding or removing material that you could shift the equilibrium? Explain why and in what direction this would shift equilibrium. (2 points)

By adding heat or removing heat, the reaction will shift depending on whether it is endothermic or exothermic. If the reaction is endothermic, add heat to shift the reaction to the products (to the right). If the reaction is exothermic, remove heat to shift the reaction to the products (to the right). Because both sides have the same number of moles, changing the volume or pressure will not push the reaction one way or the other.

Total of 2 points: 1 point for stating a correct shift. 1 point for valid explanation. Must have either discussed how and/or why temperature change would cause a shift OR how and/or why pressure and volume changes wouldn’t cause a shift. Only partial credit given if there was no analysis after the student's statement that temperature would cause shift or that pressure/volume wouldn't cause shift. Full credit given if assumptions were made about the nature of the reaction (for example: if the student stated that they thought the reaction was endothermic and then stated a correct analysis on temperature change). No credit given if the response stated that there is no way to shift the equilibrium.

2. You have 100 mL of 0.2 M formic acid, HCOOH, and 100 mL of 0.1 M potassium hydroxide, KOH. You mix these to solution to make a final aqueous solution.

A. Write the balanced chemical equation for this neutralization reaction. (2 points)

Possible ways to write the equation:
- HCOOH (aq) + KOH (aq) → HCOO⁻ (aq) + K⁺ (aq) + H₂O (l)
- HCOOH (aq) + KOH (aq) → HCOOK (aq) + H₂O (l)
- HCOOH (aq) + K⁺ (aq) + OH⁻ (aq) → HCOO⁻ (aq) + K⁺ (aq) + H₂O (l)
- HCOOH (aq) + OH⁻ (aq) → HCOO⁻ (aq) + H₂O (l)

Total of 2 points: 1 point for correct reaction (correct products and reactants). 1 point for correctly balancing.

B. Sketch a molecular perspective for each of these three solutions indicating only the major species present in the solution besides the water. If you have multiple species make sure your drawings attempt to reflect the relative ratios. (3 points)

BE SURE TO COMPLETE BOTH THE FRONT AND BACK
Total of 3 points: 1 point for showing KOH completely dissociated and HCOOH remained mostly/all undissociated. 1 point for showing correct conjugate base in the final solution. 1 point for showing that not all weak acid is used up or dissociated in solution.

C. Write out a balanced chemical equation for the equilibrium reaction that describes the final solution. (3 points)

Some possibilities:

\[
\begin{align*}
\text{HCOO}^- \text{(aq)} + \text{H}_2\text{O} \; (l) & \leftrightarrow \text{HCOOH} \text{(aq)} + \text{OH}^- \text{(aq)} \\
\text{HCOO}^- \text{(aq)} + \text{K}^+ \text{(aq)} + \text{H}_2\text{O} \; (l) & \leftrightarrow \text{HCOOH} \text{(aq)} + \text{OH}^- \text{(aq)} + \text{K}^+ \text{(aq)} \\
\text{HCOOH} \text{(aq)} + \text{H}_2\text{O} \; (l) & \leftrightarrow \text{HCOO}^- \text{(aq)} + \text{H}_3\text{O}^+ \text{(aq)} \\
\text{HCOOH} \text{(aq)} & \leftrightarrow \text{H}^+ \text{(aq)} + \text{HCOO}^- \text{(aq)}
\end{align*}
\]

Total of 3 points: 1 point for correct showing acid or base reacting with water. 2 points for the correctly written products. Full credit given if this chemical equation accurately reflects the “final solution” mixture drawn in part B even if the student was incorrect in part B. Only partial credit given if the equation was not balanced.

D. What is the pH of the final solution? (4 points)

\[
\begin{align*}
\text{HCOOH} + \text{OH}^- & \leftrightarrow \text{HCOO}^- + \text{H}_2\text{O} \\
0.02\text{mol} & \quad 0.01\text{mol} \quad 0 \quad \text{--------} \\
-0.01\text{mol} & \quad -0.01\text{mol} \quad +0.01\text{mol} \quad \text{--------} \\
0.01\text{mol} & \quad 0 \quad 0.01\text{mol} \quad \text{--------}
\end{align*}
\]

You have a mixture of a weak acid and its conjugate base remaining in solution. You should use the Henderson-Hasselbalch equation to solve.

You can actually keep everything in moles because the volume factor in the concentrations will drop out in this case. For the sake of thoroughness, new concentrations were calculated here anyway.

\[
\begin{align*}
[HCOOH] & = \frac{0.01\text{mol}}{0.3\text{L}} = 0.033\text{M} \\
[HCOO^-] & = \frac{0.01\text{mol}}{0.3\text{L}} = 0.033\text{M} \\
pH & = pKa + \log \left( \frac{[A^-]}{[HA]} \right) = -\log(Ka) + \log \left( \frac{[HCOO^-]}{[HCOOH]} \right) \\
pH & = -\log(1.8\times10^{-4}) + \log \left( \frac{0.033\text{M}}{[HCOOH]} \right) \\
pH & = 3.74 + \log \left( \frac{0.033\text{M}}{[HCOOH]} \right)
\end{align*}
\]

Total of 4 points: 4 points for correct answer. If partial credit needed: 1 point for correct neutralization set-up (the reaction must be perfect, the reaction must go 100% to products and the RICE table must be in moles). 1 point for correct “end” values. 1 point for HH equation. 1 point for correct answer.
E. If you wanted to make the final solution to have a pH = 5.0, what could you add to the solution? (2 points)

More base would need to be added to the solution to raise the pH from 3.74 to 5.0.

Total of 2 points: 2 points for valid response based on their pH from part D. If the calculated pH is higher than pH 5, valid responses that would lower the pH were accepted. No points given for removing anything.

F. How many moles of the compound from part D would you add to the solution to make the pH = 5.0? (2 points. We are asking just how many moles of the compound you would add, not how much of a solution. You can assume volume changes will be negligible.)

Total of 2 points: 2 points for valid response based on their response from part E. For partial credit: 1 point for correct work/set-up, 1 point for correct answer based on work. Any incorrect work from the previous work was considered and incorporated in the student's response in part F.

The best solution is to add strong base to make more of the weak base species.

\[
\begin{align*}
\text{HCOOH} + \text{OH}^- & \rightarrow \text{HCOO}^- + \text{H}_2\text{O} \\
0.01\text{mol} & \quad \text{X mol} & \quad 0.01\text{mol} & \quad \text{-----} \\
-\text{x} & \quad -\text{x} & \quad +\text{x} & \quad \text{-----} \\
0.01-\text{x} & \quad 0 & \quad 0.01+\text{x} & \quad \text{-----}
\end{align*}
\]

Here we know x is probably a pretty big number to change the pH that much so we actually need to solve for it! We have a buffer solution so we will use Henderson-Hasselbalch to help. The concentrations of the weak acid and weak base have the same volume values which will cancel out in their ratio anyway, so we can keep everything in moles in this case.

\[
\begin{align*}
5.00 &= pH = pKa + \log \left(\frac{[A^-]}{[HA]}\right) = -\log(Ka) + \log \left(\frac{[HCOO^-]}{[HCOOH]}\right) = -\log(1.8 \times 10^{-4}) + \log \left(\frac{0.01+X}{0.01-X}\right) \\
5.00 &= 3.74 + \log \left(\frac{0.01+X}{0.01-X}\right) \\
1.26 &= \log \left(\frac{0.01+X}{0.01-X}\right) \\
10^{1.26} &= \frac{0.01+X}{0.01-X} \\
0.182 - 18.2X &= 0.01 + X \\
0.172 &= 19.2X \\
X &= 0.009\text{mol}
\end{align*}
\]

The first option is to add 0.009 mol of a strong base like NaOH or KOH. See next page for second option.

BE SURE TO COMPLETE BOTH THE FRONT AND BACK
OR you could’ve just dumped in a bunch of HCOO\textsuperscript{−} as a salt. Here you wouldn’t change the amount of HCOOH you have (like in the previous solution above), but just the HCOO\textsuperscript{−}.

\[ 5.00 = pH = pK_a + \log \left( \frac{[A^-]}{[HA]} \right) = -\log(K_a) + \log \left( \frac{[HCOO^-]}{[HCOOH]} \right) = -\log(1.8 \times 10^{-4}) + \log \left( \frac{0.01 + X}{0.01} \right) \]

\[ 5.00 = 3.74 + \log \left( \frac{[0.01 + X]}{[0.01]} \right) \]

\[ 1.26 = \log \left( \frac{[0.01 + X]}{[0.01]} \right) \]

\[ 10^{1.26} = 18.2 = \frac{[0.01 + X]}{[0.01]} \]

\[ 0.182 = 0.01 + X \]

\[ 0.172\text{mol} = X \]

The second option is to add 0.172mol of the weak conjugate base HCOO\textsuperscript{−}.