Question 1 (10 points)

Answer the following questions that relate to the chemistry of halogen oxoacids.

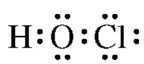
(a) Use the information in the table below to answer part (a)(i).

Acid	K_a at 298 K
HOCl	2.9×10^{-8}
HOBr	2.4×10^{-9}

(i) Which of the two acids is stronger, HOCl or HOBr ? Justify your answer in terms of K_a .

HOCl is the stronger acid because its K_a value is greater than the K_a value of HOBr.	One point is earned for the correct answer with justification.

(ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).

	One point is earned for a correct diagram.

(iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid that you identified in part (a)(i). Justify your prediction in terms of chemical bonding.

HOI is a weaker acid than HOCl because the O–H bond in HOI is stronger than the O–H bond in HOCl. The lower electronegativity (electron-drawing ability) of I compared with that of Cl results in an electron density that is higher (hence a bond that is stronger) between the H and O atoms in HOI compared with the electron density between the H and O atoms in HOCl. **OR** The conjugate base OCl^- is more stable than OI^- because Cl, being more electronegative, is better able to accommodate the negative charge.	One point is earned for predicting that HOI is a weaker acid than HOCl <u>and</u> stating that iodine has a lower electronegativity than chlorine **and EITHER** • stating that this results in a stronger O–H bond in HOI **OR** • stating that this decreases the stability of the OI^- ion in solution.

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Question 1 (continued)

(b) Write the equation for the reaction that occurs between hypochlorous acid and water.

$HOCl + H_2O \rightleftarrows OCl^- + H_3O^+$ **OR** $HOCl \rightleftarrows OCl^- + H^+$	One point is earned for the correct equation.

(c) A 1.2 M NaOCl solution is prepared by dissolving solid NaOCl in distilled water at 298 K. The hydrolysis reaction $OCl^-(aq) + H_2O(l) \rightleftarrows HOCl(aq) + OH^-(aq)$ occurs.

(i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between $OCl^-(aq)$ and $H_2O(l)$.

$K_b = \dfrac{[HOCl][OH^-]}{[OCl^-]}$	One point is earned for the correct expression.

(ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.

$K_b = \dfrac{K_w}{K_a} = \dfrac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = \mathbf{3.4 \times 10^{-7}}$	One point is earned for the correct value with supporting work.

(iii) Calculate the value of $[OH^-]$ in the 1.2 M NaOCl solution at 298 K.

	$[OCl^-]$	$[HOCl]$	$[OH^-]$
initial value	1.2	0	≈ 0
change	$-x$	x	x
equilibrium value	$1.2 - x$	x	x

One point is earned for the correct setup.

$$K_{hyd} = 3.4 \times 10^{-7} = \frac{[OH^-][HOCl]}{[OCl^-]} = \frac{(x)(x)}{(1.2 - x)} \approx \frac{x^2}{1.2}$$

$$\Rightarrow (1.2)(3.4 \times 10^{-7}) = x^2 \Rightarrow$$

$$x = [OH^-] = \mathbf{6.4 \times 10^{-4}}\ M$$

One point is earned for the correct answer with supporting calculations.

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Question 1 (continued)

(d) A buffer solution is prepared by dissolving some solid NaOCl in a solution of HOCl at 298 K. The pH of the buffer solution is determined to be 6.48.

(i) Calculate the value of $[H_3O^+]$ in the buffer solution.

$[H^+] = 10^{-6.48} = \mathbf{3.3 \times 10^{-7}}\ \boldsymbol{M}$	One point is earned for the correct value.

(ii) Indicate which of $HOCl(aq)$ or $OCl^-(aq)$ is present at the higher concentration in the buffer solution. Support your answer with a calculation.

$[H^+] = 3.3 \times 10^{-7}\ M$ and K_a for HOCl $= 2.9 \times 10^{-8}$ $K_a = \frac{[H^+][OCl^-]}{[HOCl]}$ $2.9 \times 10^{-8} = \frac{(3.3 \times 10^{-7})[OCl^-]}{[HOCl]}$ $\frac{[OCl^-]}{[HOCl]} = \frac{2.9 \times 10^{-8}}{3.3 \times 10^{-7}} = 0.088 \Rightarrow [HOCl] > [OCl^-]$	One point is earned for the correct answer with supporting buffer calculations.

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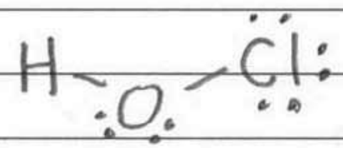
ADDITIONAL PAGE FOR ANSWERING QUESTION 1

a) i) HOCl is the stronger acid. The K_a valve of HOCl is greater than the K_a of HOBr. Since K_a = Product of concentrations of dissociated ions divided by the concentration of the acid (Thus K_a for HOCl = $\frac{[H^+][OCl^-]}{[HOCl]}$), a larger K_a valve means that there are more dissociated ions present. Thus, HOCl dissociates more making it the stronger acid.

ii) 

iii) HOI is weaker than HOCl. The polar bond between the halogen and the O in both morecules pulls electrons away from the H in the O-H bond. The more the electrons are pulled away from the H, the easier the H dissociates and becomes H^+. Cl is more electronegative than I. Therefore it pulls more on the electrons. Thus, the H in HOCl dissociates more easily than in HOI making HOI a weaker acid than HOCl.

b) $HOCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OCl^-_{(aq)}$

c) i) $K_{eq} = \frac{[HOCl_{(aq)}][OH^-_{(aq)}]}{[OCl^-_{(aq)}]}$

ii) $(K_a)(K_b) = K_w$

$(2.9\times10^{-8})(K_b) = 1.0\times10^{-14}$

$1.0\times10^{-14} / 2.9\times10^{-8} = K_b$

$K_b = 3.4\times10^{-7}$

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

iii)

	OCl^-	$HOCl$	OH^-
I	1.2M	0M	0M
C	$-x$	$+x$	$+x$
E	$(1.2-x)$M	xM	xM

$[HOCl] = [OH^-]$

$$3.4\times10^{-7} = \frac{[HOCl][OH^-]}{[OCl^-]}$$

$$3.4\times10^{-7} = \frac{(x)(x)}{(1.2-x)}$$

$$\sqrt{(3.4\times10^{-7})(1.2-x)} = x = 6.4\times10^{-4}$$

$$\boxed{[OH^-] = 6.4\times10^{-4}\,M}$$

d) i) $pH = -\log[H_3O^+]$

$10^{-pH} = [H_3O^+]$

$10^{-6.48} = [H_3O^+]$

$$\boxed{[H_3O^+] = 3.31\times10^{-7}\,M}$$

ii) $pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$

$[base] = [OCl^-]$
$[acid] = [HOCl]$

$6.48 = -\log(2.9\times10^{-8}) + \log\left(\frac{[base]}{[acid]}\right)$

$6.48 = 7.54 + \log\left(\frac{[base]}{[acid]}\right)$

$-1.06 = \log\left(\frac{[base]}{[acid]}\right)$

$10^{-1.06} = ([base]/[acid])$

$.087 = [base]/[acid]$

$(.087)[acid] = [base]$

$[acid] > [base]$

$[HOCl] > [OCl^-]$

HOCl is present in higher concentration

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

(a)(i) HOCl is a stronger acid than HOBr. The K_a value for HOCl is greater (it has a smaller negative exponent) than the K_a value for HOBr. A larger K_a value signifies a stronger acid, and since $pH = -\log(K_a)$ a larger K_a value results in a lower pH which is more acidic.

(ii) HOCl:

H — Ö — C̤̈l :

(iii) Acids want to donate a proton (H^+). So a strong acid readily gives up a proton. In order to give up a proton, the hydrogen bond must be fairly weak. Since Cl is more electronegative than I, the Cl can pull electrons closer to itself better, strengthening the O–Cl bond and therefore weakening the H–O bond. The I can't pull as strong as Cl so its H–O bond is stronger than in HOCl, and therefore it won't break the hydrogen bond easily to lose H^+. Therefore HOI is a weaker acid than HOCl.

(b) $HOCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OCl^-(aq)$

(c)(i) ~~[illegible]~~ $K_a = [HOCl][OH^-]$

(ii) ~~There is 1.2 M NaOCl to start with. So there is 1.2 M of the [illegible]~~

K_a of HOCl $= 2.9 \times 10^{-8}$

$K_w / K_a = K_b = 3.448 \times 10^{-7} = \frac{[HOCl][OH^-]}{[OCl^-]}$ = $K_b = 3.5 \times 10^{-7}$

(ii) there is 1.2 M OCl^- to begin with. This will decrease and the concentrations of the products will increase as equilibrium is approached.

$K_b = 3.448 \times 10^{-7} = \frac{(x)(x)}{(1.2 - x)}$ The solution for this equation is $x = 6.434 \times 10^{-4}$

Since one of the x's on the numerator represents the $[OH^-]$ concentration, $[OH^-] = 6.4 \times 10^{-4}$ M

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

(d) (i) A pH of 6.48 can be written also as a concentration of H^+ in solution:

$pH = -\log[H^+]$

$6.48 = -\log[H^+]$

$-6.48 = \log[H^+]$, so 3.311×10^{-7} M $= [H^+]$ so $[H_3O^+] = 3.3 \times 10^{-7}$ M

(ii) Since a pH of 6.48 is acidic, there will be a higher concentration of $[H^+]$ as opposed to $[OH^-]$. Since HOCl can produce H_3O^+ to make the solution acidic, there is more HOCl than OCl^-.

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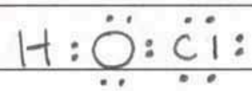
ADDITIONAL PAGE FOR ANSWERING QUESTION 1

(a)(i) HOCl is stronger because it has a lower Ka at 298K. When the Ka is smaller it means that the pH is smaller and a smaller pH signifies a stronger acid.

(ii)



(iii) HOI is a weaker acid than HOCl. HOCl has a higher electronegativity and ionization energy so it bonds stronger with the other elements in the compound. The stronger the bonds, the stronger the acid and HOI is not as strong as HOCl

(b) $HOCl + H_2O \rightarrow ClO^- + H_3O^+$

(c)(i) $K_{eq} = \frac{[HOCl][OH^-]}{[OCl^-]}$

(ii) $OCl^- \rightarrow HOCl + OH^-$

	OCl^-	$HOCl$	OH^-
init.	1.2 M	0	0
change	-.063	+.063	+.063
equil.	1.137	.063	.063

$K_{eq} = \frac{(.063)^2}{1.137}$

$3.07 \times 10^{-3} = K_{eq}$

(iii) 10 ^ (-1.2) = .063

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ADDITIONAL PAGE FOR ANSWERING QUESTION 1

(d)(i) 10^(-6.48)

$3.3 \times 10^{-7} = [H_3O^+]$

(ii) HOCl is present at the higher concentration

14 - 6.48 = 7.52

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AP® CHEMISTRY
2009 SCORING COMMENTARY

Question 1

Overview

This question assessed the breadth of students' understanding of weak acid/weak base/buffer equilibria in aqueous solution and their ability to apply the concepts to solve problems. In part (a)(i) students were required to interpret given K_a values of two halogen oxoacids to determine their relative acid strengths. In part (a)(ii) students were asked to draw a complete Lewis electron-dot diagram for one of the halogen oxoacids, and in part (a)(iii) they had to predict and justify the relative strength of a third oxoacid in terms of principles of chemical bonding. In part (b) students were asked to write a balanced chemical equation for the reaction of a weak acid in aqueous solution. In part (c) they were required to write a hydrolysis expression, calculate the value of K_b (hydrolysis equilibrium constant) from the given value of K_a, and calculate $[OH^-]$ for a solution of the conjugate base of one of the oxoacids of given concentration. Finally, in part (d) students had to determine $[H_3O^+]$ in a buffer solution of given pH and to apply the definition of K_a (or the Henderson–Hasselbalch equation) to determine the relative concentrations of HOCl and OCl^- in the buffer solution.

Sample: 1A
Score: 10

This response earned all 10 points: 1 for part (a)(i), 1 for part (a)(ii), 1 for part (a)(iii), 1 for part (b), 1 for part (c)(i), 1 for part (c)(ii), 2 for part (c)(iii), 1 for part (d)(i), and 1 for part (d)(ii).

Sample: 1B
Score: 8

The point was not earned in part (c)(i) because the denominator is omitted from the expression. The point was not earned in part (d)(ii) because the justification is incorrect.

Sample: 1C
Score: 4

The point was not earned in part (a)(i) because the response incorrectly states the relative magnitudes of the K_a values given. The point was not earned in part (a)(iii) because the statement that "[t]he stronger the bonds, the stronger the acid" is vague and incorrect. None of the possible 3 points was earned in parts (c)(ii) and (c)(iii). The point was not earned in part (d)(ii) because the justification is incorrect.

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