

AP[®] CHEMISTRY
2009 SCORING GUIDELINES

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

$\text{H}:\ddot{\text{O}}:\ddot{\text{Cl}}:$	One point is earned for a correct diagram.
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(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.

<p>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.</p> <p>OR</p> <p>The conjugate base OCl^- is more stable than OI^- because Cl, being more electronegative, is better able to accommodate the negative charge.</p>	<p>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</p> <ul style="list-style-type: none"> • stating that this results in a stronger O–H bond in HOI <p>OR</p> <ul style="list-style-type: none"> • 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.

$\text{HOCl} + \text{H}_2\text{O} \rightleftharpoons \text{OCl}^- + \text{H}_3\text{O}^+$ <p style="text-align: center;">OR</p> $\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$	One point is earned for the correct equation.
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(c) A 1.2 M NaOCl solution is prepared by dissolving solid NaOCl in distilled water at 298 K. The hydrolysis reaction $\text{OCl}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HOCl}(aq) + \text{OH}^-(aq)$ occurs.

(i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between $\text{OCl}^-(aq)$ and $\text{H}_2\text{O}(l)$.

$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}$	One point is earned for the correct expression.
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(ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.

$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.4 \times 10^{-7}$	One point is earned for the correct value with supporting work.
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(iii) Calculate the value of $[\text{OH}^-]$ in the 1.2 M NaOCl solution at 298 K.

<table border="1" style="margin-left: auto; margin-right: auto; border-collapse: collapse; text-align: center;"> <tr> <td style="width: 20%;"></td> <td style="width: 20%;">[OCl⁻]</td> <td style="width: 20%;">[HOCl]</td> <td style="width: 20%;">[OH⁻]</td> </tr> <tr> <td>initial value</td> <td>1.2</td> <td>0</td> <td>≈ 0</td> </tr> <tr> <td>change</td> <td>-x</td> <td>x</td> <td>x</td> </tr> <tr> <td>equilibrium value</td> <td>1.2 - x</td> <td>x</td> <td>x</td> </tr> </table> $K_{hyd} = 3.4 \times 10^{-7} = \frac{[\text{OH}^-][\text{HOCl}]}{[\text{OCl}^-]} = \frac{(x)(x)}{(1.2 - x)} \approx \frac{x^2}{1.2}$ $\Rightarrow (1.2)(3.4 \times 10^{-7}) = x^2 \Rightarrow$ $x = [\text{OH}^-] = 6.4 \times 10^{-4} M$		[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. One point is earned for the correct answer with supporting calculations.
	[OCl ⁻]	[HOCl]	[OH ⁻]														
initial value	1.2	0	≈ 0														
change	-x	x	x														
equilibrium value	1.2 - x	x	x														

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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 $[\text{H}_3\text{O}^+]$ in the buffer solution.

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

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