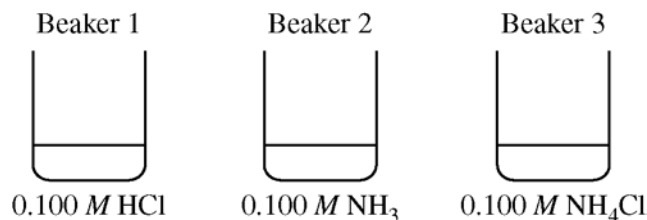


AP[®] CHEMISTRY
2011 SCORING GUIDELINES

Question 1



1. Each of three beakers contains 25.0 mL of a 0.100 M solution of HCl, NH₃, or NH₄Cl, as shown above. Each solution is at 25°C.

(a) Determine the pH of the solution in beaker 1.

Justify your answer.

$\text{pH} = -\log[\text{H}^+] = -\log(0.100) = 1.000$	<p style="text-align: center;">1 point is earned for the correct pH.</p>
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(b) In beaker 2, the reaction $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ occurs. The value of K_b for $\text{NH}_3(\text{aq})$ is 1.8×10^{-5} at 25°C.

(i) Write the K_b expression for the reaction of $\text{NH}_3(\text{aq})$ with $\text{H}_2\text{O}(\text{l})$.

$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$	<p style="text-align: center;">1 point is earned for the correct expression.</p>
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(ii) Calculate the $[\text{OH}^-]$ in the solution in beaker 2.

<p>Let $[\text{OH}^-] = x$, then $K_b = \frac{(x)(x)}{(0.100 - x)}$</p> <p>Assume that $x \ll 0.100 \text{ M}$, then</p> $1.8 \times 10^{-5} = \frac{x^2}{0.100} \Rightarrow x = [\text{OH}^-] = 1.3 \times 10^{-3} \text{ M}$	<p style="text-align: center;">1 point is earned for the correct setup. 1 point is earned for the correct answer.</p>
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(c) In beaker 3, the reaction $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ occurs.

(i) Calculate the value of K_a for $\text{NH}_4^+(\text{aq})$ at 25°C.

$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$	<p style="text-align: center;">1 point is earned for the correct answer.</p>
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Question 1 (continued)

- (ii) The contents of beaker 2 are poured into beaker 3 and the resulting solution is stirred. Assume that volumes are additive. Calculate the pH of the resulting solution.

<p>In the resulting solution, $[\text{NH}_3] = [\text{NH}_4^+]$;</p> $K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$ <p>Thus $[\text{H}_3\text{O}^+] = 5.6 \times 10^{-10}$; $\text{pH} = -\log(5.6 \times 10^{-10}) = 9.25$</p>	<p>1 point is earned for noting that the solution is a buffer with $[\text{NH}_3] = [\text{NH}_4^+]$.</p> <p>1 point is earned for the correct pH.</p>
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- (d) The contents of beaker 1 are poured into the solution made in part (c)(ii). The resulting solution is stirred. Assume that volumes are additive.

- (i) Is the resulting solution an effective buffer? Justify your answer.

<p>The resulting solution is not an effective buffer. Virtually all the NH_3 in the solution formed in (c)(ii) will react with the H_3O^+ from solution 1:</p> $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$ <p>leaving mostly NH_4^+ in the final solution. Because only one member of the $\text{NH}_4^+/\text{NH}_3$ conjugate acid-base pair is left, the solution cannot buffer both base and acid.</p>	<p>1 point is earned for the correct response with an acceptable justification.</p>
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- (ii) Calculate the final $[\text{NH}_4^+]$ in the resulting solution at 25°C.

<p>moles = (volume)(molarity)</p> <p>moles H_3O^+ in sol. 1 = $(0.0250)(0.100) = 0.00250$ mol</p> <p>moles NH_3 in sol. 2 = $(0.0250)(0.100) = 0.00250$ mol</p> <p>moles NH_4^+ in sol. 3 = $(0.0250)(0.100) = 0.00250$ mol</p> <p>When the solutions are mixed, the H_3O^+ and NH_3 react to form NH_4^+, resulting in a total of 0.00500 mol NH_4^+. The final volume is the sum $(25.0 + 25.0 + 25.0) = 75.0$ mL.</p> <p>The final concentration of $\text{NH}_4^+ = (0.00500 \text{ mol}/0.0750 \text{ L}) = 0.0667 \text{ M}$</p>	<p>1 point is earned for the correct calculation of moles of NH_4^+.</p> <p>1 point is earned for the correct calculation of the final volume <u>and</u> concentration.</p>
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1A,

ADDITIONAL PAGE FOR ANSWERING QUESTION 1

1.(a) $[H^+] = [HCl] = 0.100 M$ since $HCl \rightarrow H^+ + Cl^-$
 $pH = -\log[H^+] = -\log(0.100) = \boxed{1.00}$

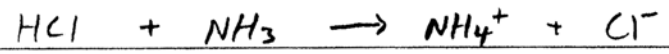
(b)(i) $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$

(b)(ii) Let $x = [NH_4^+] = [OH^-]$
 $K_b = \frac{x^2}{0.100 - x} = \frac{x^2}{0.100} = 1.8 \times 10^{-5}$
 $x = 1.3 \times 10^{-3} M$
 $[OH^-] = \boxed{1.3 \times 10^{-3} M}$

(c)(i) $K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \boxed{5.6 \times 10^{-10}}$

(c)(ii) $(0.100 M NH_3)(25.0 mL) = 2.50 \text{ mmol } NH_3$
 $(0.100 M NH_4^+)(25.0 mL) = 2.50 \text{ mmol } NH_4^+$
 $\frac{2.50 \text{ mmol } NH_3}{25.0 \text{ mL} + 25.0 \text{ mL}} = 0.0500 M NH_3$ in resulting solution
 $\frac{2.50 \text{ mmol } NH_4^+}{25.0 \text{ mL} + 25.0 \text{ mL}} = 0.0500 M NH_4^+$ in resulting solution
 $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{(0.0500)[OH^-]}{(0.0500)} = 1.8 \times 10^{-5}$
 $[OH^-] = 1.8 \times 10^{-5} M$
 $pOH = -\log[OH^-] = -\log(1.8 \times 10^{-5}) = 4.7$
 $pH = 14.0 - pOH = 14.0 - 4.7 = \boxed{9.3}$

(d)(i) $(0.100 M HCl)(25.0 mL) = 2.50 \text{ mmol } HCl$



I	2.50 mmol	2.50 mmol	2.50 mmol
C	-2.50 mmol	-2.50 mmol	+2.50 mmol
E	0	0	5.00 mmol

(d)(i) No, the resulting solution is no longer an effective buffer because there is no more NH_3 to absorb protons. Addition of more acid would cause the pH to change greatly.

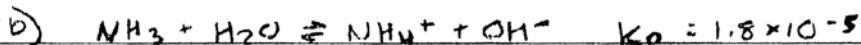
(d)(ii) From (d)(i) on the previous page, there are 5.00 mmol of NH_4^+ in the resulting solution.

$$[\text{NH}_4^+] = \frac{5.00 \text{ mmol NH}_4^+}{50.0 \text{ mL} + 25.0 \text{ mL}} = \boxed{0.067 \text{ M NH}_4^+}$$

1. $-\log .100M$

a) $pH = 1.00$

Because HCl is a strong acid, it will dissociate completely so the H^+ concentration will be equal to the concentration of HCl given



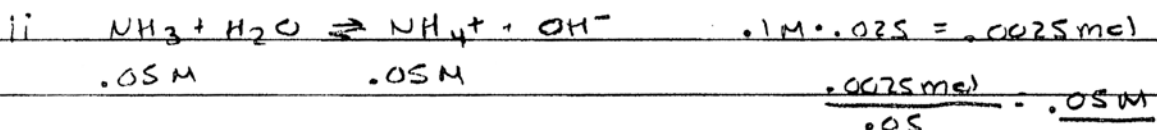
i. $1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$

ii. $1.8 \times 10^{-5} = \frac{x^2}{.1M}$ $x = .00134$

$[OH^-] = .00134M$

c) $(1.0 \times 10^{-14}) / (1.8 \times 10^{-5})$

i. $K_a = 5.6 \times 10^{-10}$



$1.8 \times 10^{-5} = \frac{.05x}{.05}$

$x = 1.8 \times 10^{-5}$ $pOH = 4.74$

$pH = 9.26$

d) i. yes, it is a buffer because

both NH_3 and NH_4^+ are common ions

with a basic pH, and they will buffer HCl.

$.075L \cdot \frac{.0025 mol}{.075L} =$

$.033M NH_3, NH_4^+$
HCl

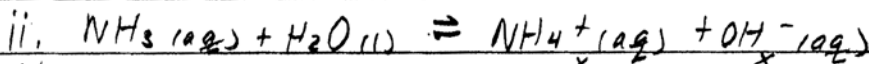
ii. $\frac{.0025 mol}{.075L} = .033M NH_4^+$

ADDITIONAL PAGE FOR ANSWERING QUESTION 1

1. a) $\text{pH} = -\log [\text{H}^+]$ ← concentration same as $[\text{HCl}]$ b/c strong acid completely dissociates

$$\text{pH} = -\log (0.1) = 1.0$$

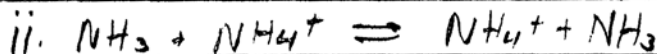
b) i. $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$



$$K_b = 1.8 \times 10^{-5} = \frac{x^2}{0.1} \rightarrow [\text{OH}^-] = 0.00134 \text{ M}$$

c) i. $K_a \times K_b = 1.0 \times 10^{-14}$

$$K_a = \frac{1.0 \times 10^{-14}}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$



$$0.1 \text{ M} \times 0.025 \text{ L} = 0.0025 \text{ moles} \quad 0.05 \text{ M}$$

$$0.05 \text{ L}$$

$$\text{pH} = -\log [0.05] = 1.3$$

d) i. Yes, the resulting solution is an effective buffer because the pH of the solution in beaker 1 is 1.0 and pH of the solution from part (c)(ii) is 1.3; these pH's are very close, so the pH when the two solutions are mixed will not change significantly.

ii. $0.1 \text{ M} \times 0.025 \text{ L} = 0.0025 \text{ moles}$

$$\frac{0.0025 \text{ moles}}{25 \text{ mL} + 25 \text{ mL} + 25 \text{ mL}} = \frac{0.0025 \text{ moles}}{0.075 \text{ L}} = 0.033 \text{ M} = [\text{NH}_4^+]$$

AP[®] CHEMISTRY

2011 SCORING COMMENTARY

Question 1

Overview

This question assessed students' understanding of and ability to solve problems and explain concepts that pertain to acid/base equilibrium and buffers. Parts of the question required calculation. Students were presented with three samples of equal volume and concentration — a strong acid, a weak base, and the conjugate acid of the weak base. Part (a) asked students to determine the pH of the solution of the strong acid and assessed their understanding of the pH scale. Part (b) required students to write the equilibrium expression for the hydrolysis reaction of the weak base and to determine the hydroxide ion concentration in the solution, given the concentration and the value of K_b for the weak base. Part (c) required students to determine the value of the K_a of the conjugate acid. Students then were told that the solutions containing the weak acid and weak base were combined and that they were to determine the pH of the resulting solution. To do so they needed to apply any of the equilibrium equations for K_b , K_a , or the Henderson-Hasselbalch equation appropriately. All three solutions were then combined, and part (d) required students to state with justification whether this solution would be an effective buffer and to determine the concentration of the weak acid in this resulting solution.

Sample: 1A

Score: 10

This response earned all available points. Part (a) earned 1 point for the correct pH, part (b)(i) earned 1 point for the correct K_b expression, and part (b)(ii) earned 2 points: 1 point for the correct setup and 1 point for the correct calculation of $[\text{OH}^-]$. Part (c)(i) earned 1 point for the calculation of the correct value of K_a , and part (c)(ii) earned 2 points for the correct calculation of the pH of the solution. Part (d)(i) earned 1 point for correctly indicating that insufficient NH_3 remained in the solution to form an effective buffer. Part (d)(ii) earned 2 points for correctly determining the $[\text{NH}_4^+]$ in the solution.

Sample: 1B

Score: 8

In part (d)(i) the statement that the solution formed would be an effective buffer did not earn the point. In part (d)(ii) 1 point was earned for calculating a consistent $[\text{NH}_4^+]$ based on an incorrect number of moles of NH_4^+ and a correct total volume.

Sample: 1C

Score: 6

In part (c)(ii) the incorrect pH calculation did not earn either of the 2 points available. In part (d)(i) the statement that the solution formed would be an effective buffer did not earn the point, and in part (d)(ii) 1 point was earned for calculating a consistent $[\text{NH}_4^+]$ based on an incorrect number of moles of NH_4^+ and a correct total volume.