2017

AP® CollegeBoard

AP Chemistry

Sample Student Responses and Scoring Commentary

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Question 3

$$N_2(g) + O_2(g) \rightleftarrows 2\ NO(g)$$

At high temperatures, $N_2(g)$ and $O_2(g)$ can react to produce nitrogen monoxide, $NO(g)$, as represented by the equation above.

(a) Write the expression for the equilibrium constant, K_p, for the forward reaction.

$K_p = \dfrac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$	1 point is earned for a correct K_p expression.

(b) A student injects $N_2(g)$ and $O_2(g)$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C. At this temperature the initial partial pressures of $N_2(g)$ and $O_2(g)$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $NO(g)$ at equilibrium is 0.122 atm. Calculate the value of K_p.

$N_2(g) + O_2(g) \rightleftarrows 2\ NO(g)$ Initial: 6.01, 1.61, 0 Change: $-x$, $-x$, $+2x$ Equilibrium: $6.01-x$, $1.61-x$, 0.122	1 point is earned for the correct equilibrium partial pressures of reactants and products (may be implicit).
$2x = 0.122$ atm $\Rightarrow$ $x = 0.0610$ atm $K_p = \dfrac{(0.122)^2}{(5.95)(1.55)} = 0.00161$	1 point is earned for the correct calculation of K_p.

Nitrogen monoxide, $NO(g)$, can undergo further reactions to produce acids, such as HNO_2, a weak acid with a K_a of 4.0×10^{-4} and a pK_a of 3.40.

(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $HNO_2(aq)$ and 0.100 M $NaOH(aq)$.

(i) Explain why the addition of 0.100 M $NaOH(aq)$ to 0.100 M $HNO_2(aq)$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $NaOH(aq)$ to the $HNO_2(aq)$.

Question 3 (continued)

NaOH will neutralize some of the HNO_2 to produce NO_2^-. The resulting solution contains a mixture of a weak acid and its conjugate base, which is a buffer solution. $$HNO_2 + OH^- \rightarrow NO_2^- + H_2O$$	1 point is earned for the recognition that the solution produced is a mixture of a weak acid and its conjugate base. 1 point is earned for the correct net ionic equation.

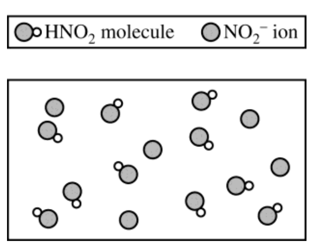
(ii) Determine the volume, in mL, of 0.100 *M* NaOH(*aq*) the student should add to 100. mL of 0.100 *M* HNO_2(*aq*) to make a buffer solution with a pH of 3.40. Justify your answer.

The student should add 50.0 mL of 0.100 *M* NaOH(*aq*). When half of the HNO_2 is converted to the conjugate base, $[HNO_2] = [NO_2^-]$, therefore the buffer has a pH equal to pK_a. OR $pH = pK_a + \log\frac{[NO_2^-]}{[HNO_2]}$, thus $pH = pK_a$ when $[HNO_2] = [NO_2^-]$	1 point is earned for the correct volume. 1 point is earned for clearly indicating a 1 to 1 ratio of HNO_2 and NO_2^- (calculation not required).

(d) A second student makes a buffer by dissolving 0.100 mol of $NaNO_2$(*s*) in 100. mL of 1.00 *M* HNO_2(*aq*). Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c) ? Justify your answer.

The buffer made by the second student is more resistant to changes in pH because it contains a higher concentration of HNO_2 and NO_2^- to react with added H^+ or OH^- ions.	1 point is earned for the correct choice and a valid justification.

(e) A new buffer is made using HNO_2(*aq*) as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40? Justify your answer.



Question 3 (continued)

The pH of the solution is less than 3.40.	1 point is earned for the correct choice.
If $[HNO_2] = [NO_2^-]$, pH = pK_a , and the pH of the solution would be 3.40. Since $[HNO_2] > [NO_2^-]$, as represented in the diagram, the solution has a pH less than 3.40. OR $\text{pH} = \text{p}K_a + \log\frac{[NO_2^-]}{[HNO_2]} \Rightarrow \text{pH} = 3.40 + \log\frac{5}{10} \Rightarrow \text{pH} = 3.10$	1 point is earned for a valid justification.

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$$N_2(g) + O_2(g) \rightleftarrows 2\,NO(g)$$

3. At high temperatures, $N_2(g)$ and $O_2(g)$ can react to produce nitrogen monoxide, $NO(g)$, as represented by the equation above.

(a) Write the expression for the equilibrium constant, K_p, for the forward reaction.

(b) A student injects $N_2(g)$ and $O_2(g)$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C. At this temperature the initial partial pressures of $N_2(g)$ and $O_2(g)$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $NO(g)$ at equilibrium is 0.122 atm. Calculate the value of K_p.

Nitrogen monoxide, $NO(g)$, can undergo further reactions to produce acids such as HNO_2, a weak acid with a K_a of 4.0×10^{-4} and a pK_a of 3.40.

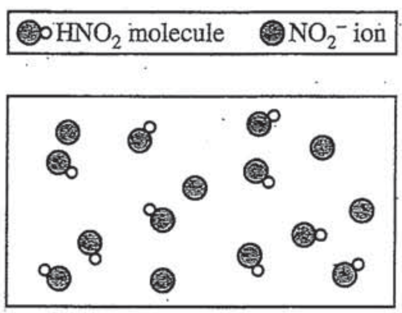
(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $HNO_2(aq)$ and 0.100 M NaOH(aq).

(i) Explain why the addition of 0.100 M NaOH(aq) to 0.100 M $HNO_2(aq)$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the NaOH(aq) to the $HNO_2(aq)$.

(ii) Determine the volume, in mL, of 0.100 M NaOH(aq) the student should add to 100. mL of 0.100 M $HNO_2(aq)$ to make a buffer solution with a pH of 3.40. Justify your answer.

(d) A second student makes a buffer by dissolving 0.100 mol of $NaNO_2(s)$ in 100. mL of 1.00 M $HNO_2(aq)$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c) ? Justify your answer.

(e) A new buffer is made using $HNO_2(aq)$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40 ? Justify your answer.



a) $K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$

b)

	N_2	O_2	NO
I	6.01	1.61	0
C	−x	−x	+2x
E	6.01−x	1.61−x	.122

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

$.122 = 2x \Rightarrow x = .061$

$P_{N_2} = 6.01 - .061 = 5.949$ atm

$P_{O_2} = 1.61 - .061 = 1.549$ atm

$K_p = (.122)^2 / (5.949)(1.549) = 1.62 \times 10^{-3}$

c) i) A buffer solution occurs when an acid and its conjugate base are both present in solution in significant amount such that the conjugate base resists added acid and the acid resists added base. When NaOH is added to HNO_2

$HNO_2 + OH^- \rightarrow H_2O + NO_2^-$

Creating significant amounts of NO_2^- and HNO_2 for a buffer solution.

ii) when pH = pKa, then $\log\left(\frac{[NO_2^-]}{[HNO_2]}\right) = 0$ according to the Henderson-Hasselbach equation. Therefore, $[NO_2^-]/[HNO_2] = 1$ and $[HNO_2] = [NO_2^-]$

# of moles of HNO_2 = .1 L (.1 M) = .01 mol HNO_2

Only half the number of moles of HNO_2 should react to create equal concentrations of HNO_2 and NO_2^-, therefore .005 mol OH^- should be added

$(.005 \text{ mol } OH^-)\left(\frac{1 \text{ mol NaOH}}{1 \text{ mol } OH^-}\right) = .005$ mol NaOH

$.1$ M NaOH $= .005$ mol NaOH / Volume $\Rightarrow$ Volume $= \frac{.005 \text{ mol}}{.1 \text{ M}} =$ .05 L or 50 mL

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d) The second student's buffer is more resistant because it has more moles of acid and conjugate base in the buffer, creating a higher buffer capacity.

e) The pH is less than 3.4 because there are twice as many moles of acid as there are conjugate base. This makes $\frac{[NO_2^-]}{[HNO_2]} = \frac{1}{2}$ and $\log(\frac{1}{2})$ is a negative number; this makes the value of $pKa + \log(\frac{[NO_2^-]}{[HNO_2]})$ less than the value of pKa, decreasing the pH.

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3B 1 of 2

$$N_2(g) + O_2(g) \rightleftarrows 2\,NO(g)$$

3. At high temperatures, $N_2(g)$ and $O_2(g)$ can react to produce nitrogen monoxide, $NO(g)$, as represented by the equation above.

(a) Write the expression for the equilibrium constant, K_p, for the forward reaction.

(b) A student injects $N_2(g)$ and $O_2(g)$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C. At this temperature the initial partial pressures of $N_2(g)$ and $O_2(g)$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $NO(g)$ at equilibrium is 0.122 atm. Calculate the value of K_p.

Nitrogen monoxide, $NO(g)$, can undergo further reactions to produce acids such as HNO_2, a weak acid with a K_a of 4.0×10^{-4} and a pK_a of 3.40.

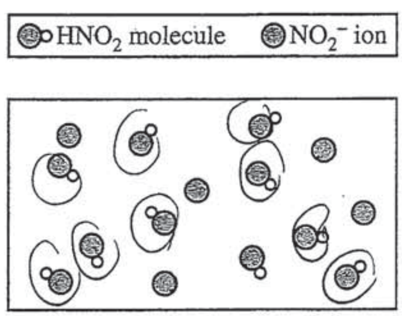
(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $HNO_2(aq)$ and 0.100 M $NaOH(aq)$.

(i) Explain why the addition of 0.100 M $NaOH(aq)$ to 0.100 M $HNO_2(aq)$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $NaOH(aq)$ to the $HNO_2(aq)$.

(ii) Determine the volume, in mL, of 0.100 M $NaOH(aq)$ the student should add to 100. mL of 0.100 M $HNO_2(aq)$ to make a buffer solution with a pH of 3.40. Justify your answer.

(d) A second student makes a buffer by dissolving 0.100 mol of $NaNO_2(s)$ in 100. mL of 1.00 M $HNO_2(aq)$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c) ? Justify your answer.

(e) A new buffer is made using $HNO_2(aq)$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40 ? Justify your answer.



$pH = pKa + \log \frac{[A^-]}{[HA]}$

$pH = 3.4 + \log \frac{5}{10}$

$pH = 3.4 - 0.30$

$pH = 3.1$

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

3. a. ~~$[NO]^2$~~ $\frac{(P_{NO})^2}{(P_{N_2})\cdot(P_{O_2})}$

b. $N_2(g) + O_2(g) \rightarrow 2NO(g)$

6.01 atm 1.61 atm 0

$-x$ $-x$ $+2x$

5.95 atm 1.55 atm 0.122 atm

↳ $0.122 = 2x = so$ $x = 0.0610$

$K_p = \frac{0.122^2}{5.95 \cdot 1.55}$, $K_p = 0.00161$

c. i. it can result in the formation of a buffer because ~~it~~ the reaction produces NO_2^-, which is the conjugate base of HNO_2: buffers ~~are~~ have both acids and their conjugate bases present, which allows them to resist change. $HNO_2 + OH^- \rightarrow NO_2^-$

ii. $pH = pKa + \log\frac{[A^-]}{[HA]}$, $pH = 3.40$ and $pKa = 3.40$ so $3.40 = 3.40 + \log\frac{[A^-]}{[HA]}$ → this means that $[A^-] = [HA]$ → $HNO_2 + OH^- \rightarrow NO_2^-$ → $0.1 - x = x \rightarrow x =$ ~~0.05000~~ 0.0500 mol OH^- →

0.1 mol, x mol; 0.1 − x, + x

$\frac{0.0500 \text{ mol } OH^-}{\text{~~x~~ mL}} = 0.100\ M$, $y = 0.500$ L or 500 mL

d. the buffer made by the ~~first~~ second student is stronger because ~~it~~ the first has OH^- in it already, so there is less ~~time to use~~ OH^- that can be added to the first ~~student's~~ student's ~~mixture~~ buffer before it ceases to be a buffer anymore

e. 10 HNO_2, 5 NO_2^- → the buffer will be less than 3.4 because the ratio of A^- to HA ions is 1/2 → $pH = pKa + \log\frac{[A^-]}{[HA]}$ → $pH = 3.4 + \log(\frac{1}{2})$ → $pH = 3.4 + -0.30$ → $pH = 3.1$ which is less than 3.4

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3C 1 of 2

$$N_2(g) + O_2(g) \rightleftarrows 2\,NO(g)$$

3. At high temperatures, $N_2(g)$ and $O_2(g)$ can react to produce nitrogen monoxide, $NO(g)$, as represented by the equation above.

(a) Write the expression for the equilibrium constant, K_p, for the forward reaction.

(b) A student injects $N_2(g)$ and $O_2(g)$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C. At this temperature the initial partial pressures of $N_2(g)$ and $O_2(g)$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $NO(g)$ at equilibrium is 0.122 atm. Calculate the value of K_p.

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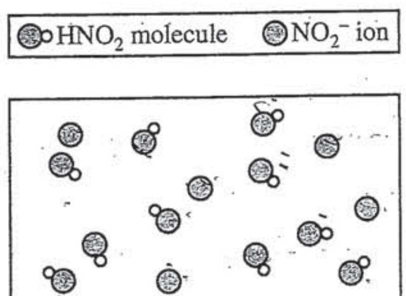
(c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $HNO_2(aq)$ and 0.100 M $NaOH(aq)$.

(i) Explain why the addition of 0.100 M $NaOH(aq)$ to 0.100 M $HNO_2(aq)$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $NaOH(aq)$ to the $HNO_2(aq)$.

(ii) Determine the volume, in mL, of 0.100 M $NaOH(aq)$ the student should add to 100. mL of 0.100 M $HNO_2(aq)$ to make a buffer solution with a pH of 3.40. Justify your answer.

(d) A second student makes a buffer by dissolving 0.100 mol of $NaNO_2(s)$ in 100. mL of 1.00 M $HNO_2(aq)$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c) ? Justify your answer.

(e) A new buffer is made using $HNO_2(aq)$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40 ? Justify your answer.



3a) $K_p = \frac{(P_{NO})^2}{(P_{N_2})(P_{O_2})}$. P_{NO} = Partial Pressure of NO. P_{N_2} = Partial Pressure of N_2. P_{O_2} = Partial Pressure of O_2

b) $K_p = \frac{(0.122\text{atm})^2}{\left(6.01 - \frac{0.122}{2}\right)\left(1.61 - \frac{0.122}{2}\right)} = 0.00162$.

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ADDITIONAL PAGE FOR ANSWERING QUESTION 3

(b)(i) A buffer solution is comprised of a weak acid ~~or base~~ and it's conjugate. As the net ionic equation for when NaOH is added is $NaOH + HNO_2 \rightarrow NaNO_2 + HOH$, a buffer is formed from the HNO_2 and $NaNO_2$ with the HNO_2 being the weak acid and the $NaNO_2$ being the conjugate.

(b)(ii) $pH = pKa \frac{(mol\ Acid)}{mol\ Base}$

$3.4 = 3.4 \frac{mol\ A}{mol\ B}$

$\frac{mol\ A}{mol\ B} = 1$, Thus one should add 100 mL of NaOH to make an equal # of moles of A & B.

(d) The one made by the first student is more resistant as it has NaOH.

(e) The pH is higher than 3.4 as there are 10 acid particle to 5 base. Using the formula $pH = pKa \frac{(mol\ acid)}{mol\ base}$, with more moles of acid, there is a higher pH.

Question 3

Overview

This question assessed students' understanding of gas phase equilibrium, the ability to calculate an equilibrium constant using equilibrium partial pressures, to identify the two major components of an acidic buffer equilibrium system and to determine the buffer capacity of a solution. The last part of the question assessed students' ability to interpret a particulate diagram representing the major species in a buffer solution and to determine the pH relative to a solution where the pH = pK_a.

In this question the Learning Objectives (LO) assessed were 6.5, 6.18, and 6.20. The Science Practices (SP) assessed were 2.2, 2.3, 4.2, and 6.4.

In part (a) students were required to write a K_p expression for a given reaction. In part (b) students had to use reaction stoichiometry and an ICE table (or its equivalent) to determine the equilibrium partial pressures of reactants and products, and then to correctly calculate the value of K_p for the system by substitution. In part (c) students were expected to analyze the preparation of a buffer solution. Part (c)(i) required students to explain, using a net ionic equation, why mixing a strong base with a weak acid could result in a buffer solution. Part (c)(ii) required students to determine the relative proportions of strong base and weak acid needed to prepare a buffer with a pH = pK_a of the weak acid. In part (d) students were required to evaluate with justification the relative buffer capacities of two similar buffers (HNO_2/NO_2^- at pH = pK_a) at different concentrations prepared by different means. In part (e) students were required to interpret a particle-level representation of a buffer solution and to state with justification whether the represented buffer had a pH greater than, less than, or equal to pK_a.

Sample: 3A
Score: 10

This response earned 10 out of 10 possible points. The student earned 1 point in part (a) for the correct setup of the K_p expression using the symbol "P" to indicate partial pressures of reactants and product at equilibrium. The student earned 2 points in part (b) for correctly determining the equilibrium partial pressures of reactants and product and substituting the partial pressures into the equilibrium-constant expression to calculate the value of K_p. The student earned 2 points in part (c)(i) for correctly identifying HNO_2 and NO_2^- as the components of the buffer and writing the balanced net ionic equation (charge and atoms) representing the neutralization of some nitrous acid with aqueous sodium hydroxide. In part (c)(ii) the student earned 2 points for correctly calculating the volume of 0.100 M NaOH required to neutralize half of the HNO_2 and for stating that when half of the nitrous acid reacts, it produces the same number of moles of the conjugate base, NO_2^-, and that the resultant solution has $[HNO_2] = [NO_2^-]$. The student earned 1 point in part (d) for choosing the buffer made by the second student and for explaining that the buffer made by the second student contains more moles of acid and conjugate base. The student earned 1 point in part (e) for correctly determining that the pH of the buffer solution in the particulate diagram is less than 3.4. The student earned the additional 1 point in part (e) for identifying the ratio of the concentrations of $[NO_2^-]$ to $[HNO_2]$ as 1:2, and log (1/2) as a negative number, which when added to 3.4 will result in a pH less than 3.4.

Sample: 3B
Score: 6

This response earned 6 out of 10 possible points. The student earned 1 point in part (a) for the correct setup of the K_p expression using the symbol "P" to indicate partial pressures of reactants and product at equilibrium. The student earned 2 points in part (b) for correctly determining the equilibrium partial pressures of reactants and

Question 3 (continued)

product and substituting the partial pressures into the equilibrium-constant expression to calculate the value of K_p. The student earned 1 point in part (c)(i) for correctly identifying the two components of a buffer as the weak acid HNO_2, and its conjugate base, NO_2^-. The second point in part (c)(i) was not earned because water is not included in the net ionic equation. No points were earned in part (c)(ii) because the student calculates an incorrect volume of NaOH(*aq*) required to neutralize half of the nitrous acid and uses the generic form of the Henderson-Hasselbalch equation without directly linking [A⁻] and [HA] to $[NO_2^-]$ and $[HNO_2]$, respectively. No point was earned in part (d) because, although the student chooses the correct buffer, the justification is not valid. The response in part (e) earned 2 points for stating that the pH of the new buffer solution would be less than 3.40 and for correctly using the Henderson-Hasselbalch equation to calculate a pH of 3.1 for the new buffer solution.

Sample: 3C
Score: 4

This response earned 4 out of 10 possible points. The student earned 1 point in part (a) for the correct setup of the K_p expression using the symbol "*P*" to indicate partial pressures of reactants and product at equilibrium. The student earned 2 points in part (b) for correctly determining the equilibrium partial pressures of reactants and product and substituting the partial pressures into the equilibrium-constant expression to calculate the value of K_p. The student earned 1 point in part (c)(i) for correctly identifying the two components of a buffer as the weak acid HNO_2, and its conjugate base, $NaNO_2$. The second point in part (c)(i) was not earned because the student writes the molecular equation instead of the net ionic equation. No points were earned in part (c)(ii). The volume of NaOH(*aq*) required to neutralize half of the nitrous acid is incorrect, and the student uses an incorrect equation. The student also incorrectly assumes that all of the weak acid reacted with the base. The point was not earned in part (d) because the student chooses the buffer made by the first student. No points were earned in part (e) because the student claims that the pH of the new buffer solution would be higher than 3.4, and the student uses an incorrect equation and states that "with more moles of acid, there is a higher pH."