

Chem 260 – Second Exam Key

On the following pages are six problems covering material in equilibrium chemistry. Read each problem carefully and think about how best to approach it before you begin work. If you aren't sure how to begin a problem, then move on; working on a new problem may stimulate an idea that helps you solve the more troublesome one. For problems requiring a written response, be sure that your answer directly and clearly answers the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation.

When working equilibrium problems, be sure to clearly state and verify any assumptions.

Note that the last two problems are worth over 50% of the total points!

Problem 1 _____/10

Problem 4 _____/7

Problem 2 _____/16

Problem 5 _____/7

Problem 3 _____/8

Problem 6 _____/24

Problem 7 _____/28

Total _____

A few constants are given here:

$$d_{\text{H}_2\text{O}} = 1.00 \text{ g/mL}$$

$$S_{\text{H}_2\text{O}} = 4.184 \text{ J/g}\cdot^\circ\text{C}$$

$$R = 8.314 \text{ J/mol}_{\text{rxn}}\cdot\text{K} \quad F = 96,485 \text{ J/V}\cdot\text{mol } e^-$$

$$K_w = 1.00 \times 10^{-14}$$

Problem 1. Will a solution of 0.10 M NH_4NO_2 be acidic, basic or neutral? Explain your reasoning in one or two sentences. Two useful equilibrium constants are:

$$K_{a,\text{HNO}_2} = 5.1 \times 10^{-4} \text{ and } K_{b,\text{NH}_3} = 1.8 \times 10^{-5}.$$

The K_a for NH_4^+ is $K_w / K_{b,\text{NH}_3}$ or $1.00 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$ and the K_b for NO_2^- is $K_w / K_{a,\text{HNO}_2}$ or $1.00 \times 10^{-14} / 5.1 \times 10^{-4} = 2.0 \times 10^{-11}$. Comparing K_a for NH_4^+ to K_b for NO_2^- shows us that NH_4^+ is a stronger acid than NO_2^- is a base; thus, *the solution is acidic*.

Problem 2. Arrange the following solutions in order of increasing pH:

0.10 M HNO_3 0.10 M HNO_2 0.10 M NaNO_2 0.10 M NH_4NO_3
 0.10 M NH_3 0.10 M NaOH 0.10 M KCl 0.50 M KOH

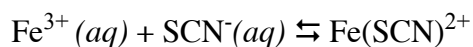
Useful equilibrium constants are in Problem 1.

Lowest pH $\rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow \rightarrow$ Highest pH

HNO_3 HNO_2 NH_4NO_3 KCl NaNO_2 NH_3 NaOH KOH

KCl is neutral and separates the acids (lower pH) from the bases. Of the three acids, HNO_3 is strong and has the lowest pH. For the two weak acids, K_a for HNO_2 is larger than that for NH_4^+ so HNO_2 will be more acidic (lower pH). NaOH and KOH are strong bases and have the largest pH values. Because the KOH solution has a higher concentration, its pH will be the largest. For the two weak bases, K_b for NH_3 is larger than that for NO_2^- ; thus, NH_3 will be more basic (higher pH) than NaNO_2 .

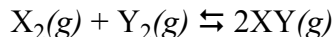
Problem 3. Ferric ion, Fe^{3+} , and thiocyanate, SCN^- , are colorless ions. When separate solutions containing these ions are mixed together, a blood-red solution of $\text{Fe}(\text{SCN})_2^{2+}$ results. The equilibrium reaction is



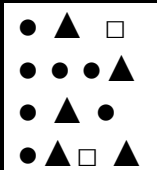
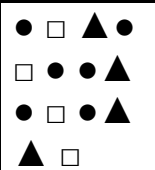
Upon adding NaNO_3 the solution's absorbance changes. Does the absorbance increase or does it decrease? Explain your reasoning in two to four sentences.

Since Na^+ and NO_3^- are not part of the equilibrium reaction, the change in absorbance cannot result from Le Châtelier's principle. The change must be due to a change in the solution's ionic strength. The presence of additional ions in solution stabilizes Fe^{3+} and SCN^- , making it harder for the complex to form. The complex's ability to dissociate is not affected. The result is a decrease in the $[\text{Fe}(\text{SCN})_2^{2+}]$ and a *decrease in absorbance*.

Problem 4. Consider the reaction

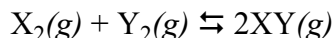


Suppose that at a particular temperature, the equilibrium position is represented by the frame on the left, where the symbol ● represents X_2 , the symbol ▲ represents Y_2 and the symbol □ represents XY . When the temperature increases, the new equilibrium position is shown by the frame on the right. Is ΔH° for the reaction greater than zero, less than zero, equal to zero, or is there insufficient information to answer. Justify your answer in one or two sentences.

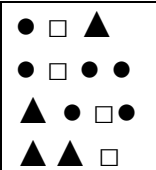
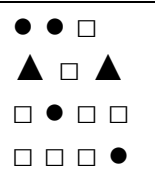
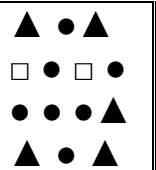
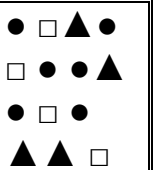
	
Left Frame	Right Frame

Increasing the temperature leads to a decrease in the molecules of X_2 ($7 \rightarrow 6$) and Y_2 ($5 \rightarrow 4$) and an increase in the molecules of XY ($2 \rightarrow 4$). Since increasing the temperature pushes the reaction to the right, heat must be a reactant and the reaction, therefore, is *endothermic*).

Problem 5. Consider the reaction



Suppose that at a particular temperature, the equilibrium position is represented by the frame on the left, where the symbol ● represents X_2 , the symbol ▲ represents Y_2 and the symbol □ represents XY . Suppose that at a particular volume, the original equilibrium position is represented by the frame on the far left. If the volume is decreased, which of the remaining frames will best represent the new equilibrium position. Clearly indicate your choice and explain your reasoning in one or two sentences.

			
Original Equilibrium	A	B	C

Because the equilibrium constant's numerator, $[\text{XY}]^2$ or $[\text{XY}] \times [\text{XY}]$, and denominator, $[\text{X}_2] \times [\text{Y}_2]$, contain an identical number of terms, a change in volume does not change the value of K_{eq} . The new equilibrium position, which has the same composition as the original equilibrium mixture, is *Frame C*.

Problem 6. Bromocresol green (HBg) is a weak acid ($pK_a = 4.9$) that is yellow in its acidic form and blue in its conjugate base form, Bg^- . As a result, a solution of the dye is green when there are roughly equivalent amounts of HBg and Bg^- . Suppose that you make a solution by dissolving 9.00×10^{-3} moles of NaBg in 1.00 L of water. What is the pH and the color of the solution?

Because Bg^- is a weak base, a solution of NaBg is basic and the pH will be *blue* because the pH will be greater than $pK_a + 1 = 4.9 + 1 = 5.9$. The pK_b for Bg^- is $14 - 4.9 = 9.1$, giving a K_b of 7.94×10^{-10} . The concentration of Bg^- is 9.00×10^{-3} M.

	Bg^-	$+ H_2O$	\rightleftharpoons	OH^-	$+ HBg$
Initial	9.00×10^{-3}	—		0	0
Change	—x	—		+x	+x
Equilibrium	$9.00 \times 10^{-3} - x$	—		x	x

Substituting into the K_b expression, making a simplifying assumption and solving

$$K_b = 7.94 \times 10^{-10} = \frac{[OH^-][HBg]}{[Bg^-]} = \frac{(x)(x)}{(9.00 \times 10^{-3} - x)} \approx \frac{x^2}{9.00 \times 10^{-3}}$$

gives a value for x of 2.67×10^{-6} (an error in the assumption of 0.03%), which is the $[OH^-]$ and $[HBg]$. The $[H_3O^+]$ is $1.00 \times 10^{-14} / 2.67 \times 10^{-6} = 3.75 \times 10^{-9}$ or a *pH of 8.43*.

To study the activity of a particular enzyme that releases H_3O^+ , you add it to your solution of NaBg. As the enzymatic reaction occurs, the color of your solution changes. What is the pH of the solution when it just turns yellow and what is the concentration of HBg? You may assume that adding the enzyme does not change the solution's volume. Explain your reasoning with precisely chosen words and appropriate calculations.

When the solution just turns yellow, the pH is at the acidic edge of bromocresol green's buffering range, which is a pH of 3.9. The question, then, is: What is the $[HBg]$ at a pH of 3.9? There are several approaches to this problem, but one is to recognize that

$$\frac{[Bg^-]}{[HBg]} = 0.1 = \frac{\text{moles } Bg^-}{\text{moles HBg}} = \frac{(\text{moles } Bg^-)_o - (\text{moles } H_3O^+)_{\text{added}}}{(\text{moles HBg})_o + (\text{moles } H_3O^+)_{\text{added}}} = \frac{9.00 \times 10^{-3} - x}{2.67 \times 10^{-6} + x}$$

because the released H_3O^+ converts some of the Bg^- to HBg. Solving for x gives a value of 8.18×10^{-3} . The total moles of HBg is $2.67 \times 10^{-6} + x$ or 8.18×10^{-3} . With a volume of 1.0 L, the concentration is 8.18×10^{-3} M.

Problem 7. A microbiologist needs to prepare a buffer with a pH of 7.00 that she can use for preparing bacterial cultures. Solutions of 0.10 M K_2HPO_4 and 0.10 M KH_2PO_4 are available. The pK_a values for H_3PO_4 are 2.15, 7.20 and 12.38.

One method of preparing the buffer is to take 0.100 L of the K_2HPO_4 solution and to add an appropriate volume of the KH_2PO_4 solution. How many mL should she use?

Because this is a buffer, we use the H-H equation; thus

$$\text{pH} = 7.00 = \text{pK}_{a2} + \log \frac{\text{moles HPO}_4^{2-}}{\text{moles H}_2\text{PO}_4^-} = 7.20 + \log \frac{(0.10 \text{ M HPO}_4^{2-})(0.100 \text{ L})}{(0.10 \text{ M H}_2\text{PO}_4^-)V}$$

where V is the volume of KH_2PO_4 . Solving for V gives a volume of 0.158 L or 158 mL.

Having prepared this buffer, will it be better at protecting against the addition of strong acid or strong base. Explain your answer in one or two sentences.

Because the buffer has more moles of the weak acid, $\text{H}_2\text{PO}_4^{2-}$, than of the weak base, HPO_4^- , it will be better at protecting against the addition of *strong base*.

What will be the pH of the buffer if the bacteria excrete 1.2×10^{-3} moles of H_3O^+ ?

Adding acid converts some of the HPO_4^{2-} to H_2PO_4^- . Using the H-H equation

$$\text{pH} = 7.20 + \log \frac{(\text{moles HPO}_4^{2-})_o - \text{moles H}_3\text{O}^+}{(\text{moles H}_2\text{PO}_4^-)_o + \text{moles H}_3\text{O}^+} = 7.20 + \log \frac{0.0100 - 1.2 \times 10^{-3}}{0.0158 + 1.2 \times 10^{-3}} = 6.91$$

shows that the *pH is 6.91*.

What is the original buffer's capacity to neutralize strong base? Report your answer as the amount, in grams, of NaOH that can be neutralized by the buffer.

Adding strong base converts some of the H_2PO_4^- to HPO_4^{2-} . The buffer's capacity is reached when the ratio of HPO_4^{2-} to H_2PO_4^- is 10:1; thus

$$\frac{\text{moles HPO}_4^{2-}}{\text{moles H}_2\text{PO}_4^-} = 10 = \frac{0.0100 + x}{0.0158 - x}$$

where x is the moles of NaOH. Solving for x gives 1.35×10^{-2} moles of NaOH, which is equivalent to 0.54 g of NaOH.