

Unit Exam: Equilibrium Chemistry

On the following pages are problems that consider equilibrium chemistry in the context of chemical or biochemical systems. Read each question carefully and consider how you will approach it before you put pen or pencil to paper. If you are unsure how to answer a question, then move on to another question; working on a new question may suggest an approach to a question that is more troublesome. If a question requires a written response, be sure that you answer in complete sentences and that you directly and clearly address the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation and that work is relevant to the question.

Problem	Points	Maximum	Problem	Points	Maximum
1	9.1	11	4	17.3	20
2	8.9	11	5	18.9	23
3	8.0	11	6	19.0	24
			Total	81.2	100

high score	scores 100–90	scores 89–80	scores ≤ 79
98	6	7	8

A few constants are given here; other information is included within individual problems.

- density (d) of water is 1.00 g/mL
- specific heat (S) of water is 4.184 J/g \cdot $^{\circ}$ C
- the gas constant (R) is 8.314 J/mol_{rxn} \cdot K
- Faraday's constant (F) is 96,485 C/mol e⁻ or 96,485 J/V \cdot mol e⁻
- water's dissociation constant (K_w) is 1.00×10^{-14}

!!Special Note on Solutions to Equilibrium Problems!!

There are many options available to you when solving an equilibrium problem, including a rigorous algebraic solution, making an assumption to simplify the algebra, or using a calculator's ability to solve the equation. Each method requires some care and attention on your part; at a minimum this means that:

- *if you solve the problem rigorously, be sure your algebraic work is neat and easy to follow, and that you report all possible solutions before you identify the chemically meaningful solution*
- *if you make an assumption, be sure to test the validity of that assumption before you accept and report a final answer*
- *if you use your calculator's solver function, be sure to indicate the exact function you entered into your calculator and report all possible solutions before you identify the chemically meaningful solution*

Part A: Three Problems With Short Written Answers and/or With Short Calculations

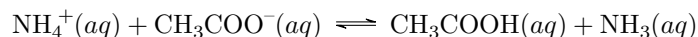
Problem 1. Good buffers (here Good is Norman Good, who was a plant biologist at Michigan State University) are a set of buffering reagents whose properties make them well-suited for work in physiological systems. One such Good buffer is piperazine–N,N'–bis(2-ethanesulfonic acid), which commonly is referred to as PIPES. Its weak acid form is HPIPES⁺ and it has a p*K*_a of 6.76 at 25°C. Suppose you prepare a PIPES buffer with a pH of 7.00. Does your buffer have a greater capacity to neutralize strong acid or strong base, or does it have an equal ability to neutralize both strong acid and strong base. Explain your answer in no more than three sentences.

Answer. Because the buffer's pH is greater than the p*K*_a of its weak acid, we know that we have more of the weak base than we do of the weak acid. An excess of weak base means that we have more capacity to neutralize strong acid than we do to neutralize strong base.

Problem 2. As is the case with all buffer salts, the p*K*_a of HPIPES⁺ changes with temperature, with a value of 6.66 reported at a temperature of 37°C and a value of 6.94 at a temperature of 4°C. What do these values imply about the sign of ΔH for its acid dissociation reaction? Is $\Delta H > 0$, $\Delta H < 0$, $\Delta H = 0$, or is there insufficient information to determine its sign? Explain your answer in no more than three sentences.

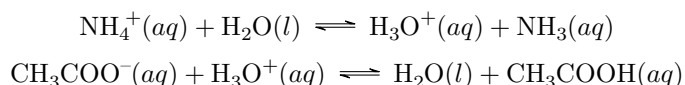
Answer. The p*K*_a increases as the temperature decreases, which means that the *K*_a is smaller at lower temperatures. A smaller *K*_a means that a decrease in temperature shifts the reaction toward the reactants to produce heat; thus, heat is a reactant and the reaction is endothermic with $\Delta H > 0$.

Problem 3. Ammonium acetate is an interesting compound because it consists of both a weak acid, NH₄⁺, and a weak base, CH₃COO[−]. When you dissolve CH₃COONH₄ in water the following equilibrium reaction determines the solution's composition.



Given that the *K*_a for NH₄⁺ is 5.6×10^{-10} and that the *K*_a for CH₃COOH is 1.8×10^{-5} , what is the equilibrium constant for the reaction above? Given your equilibrium constant, does a solution of ammonium acetate have a greater concentration of NH₃ or of NH₄⁺? Explain your answer in one sentence.

Answer. Because the reaction is not an equilibrium reaction with a published value for *K*, we have to find a set of reactions we can add together to give the overall reaction. One possible set of reaction is



The equilibrium constant for the first reaction is *K*_a for NH₄⁺ and the equilibrium constant for the second reaction is (*K*_a)^{−1} for CH₃COOH; thus the equilibrium constant is

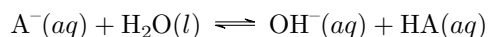
$$K = \frac{K_{a, \text{NH}_4^+}}{K_{a, \text{CH}_3\text{COOH}}} = \frac{5.6 \times 10^{-10}}{1.8 \times 10^{-5}} = 3.1 \times 10^{-5}$$

Because the equilibrium constant is less than one, we know that there are more reactants than products, which means that there is more NH₄⁺ than there is NH₃.

Part B: Three Problems With More Involved Calculations

Problem 4. Most soaps contain long-chain fatty acids in the form of sodium salts, one example of which is sodium stearate, $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$. A solution is prepared by dissolving 5.0 g of $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$ in 1.00 L of water. The pH of the resulting solution is measured as 8.55. What is K_b for the stearate ion?

Answer. Stearate is a weak base, which we will represent here as A^- , and it makes the solution basic by the reaction



The initial concentration of A^- is 0.0163 mol/L (5.0 g of $\text{CH}_3(\text{CH}_2)_{16}\text{COONa}$, which has a molar mass of 306.5 g/mol, dissolved in 1.00 L of solution). The equilibrium concentration of OH^- is 3.55×10^{-6} mol/L (from pOH of $14 - 8.55 = 5.45$ and $\text{pOH} = -\log[\text{OH}^-]$). With these values, we complete an ICE table

	$\text{A}^-(aq) +$	$\text{H}_2\text{O}(l)$	\rightleftharpoons	$\text{OH}^-(aq) +$	$\text{HA}(aq)$
initial	0.0163	–		0	0
change	-3.55×10^{-6}	–		$+3.55 \times 10^{-6}$	$+3.55 \times 10^{-6}$
equilibrium	$0.163 - 3.55 \times 10^{-6}$	–		3.55×10^{-6}	3.55×10^{-6}

Substituting the equilibrium concentrations into the K_b expression gives its value as

$$K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} = \frac{(3.55 \times 10^{-6})^2}{0.163 - 3.55 \times 10^{-6}} = 7.73 \times 10^{-10}$$

What is the $\text{p}K_a$ for stearic acid, the conjugate weak acid of the stearate ion?

Answer. The K_a for stearic acid is equal to K_w/K_b , stearate, or 1.29×10^{-5} . The $\text{p}K_a$ is $-\log(1.29 \times 10^{-5})$, or 4.89.

Problem 5. Commercial grape-flavored fruit juice powders usually include a mixture of tartaric acid, $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$, and potassium tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, to fix the pH of the juice when the powder is dissolved in water. Suppose you work for a company that manufactures this beverage and are asked to devise a formulation with the following properties: when a package of the powdered mixture is added to 750 mL of water, the resulting pH is 3.20 and the total concentration of buffering agents is 0.100 M. How many grams of $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ and of $\text{KHC}_4\text{H}_4\text{O}_6$ do you need in each package of the powdered mixture? The K_a for tartaric acid is 9.20×10^{-4} .

Answer. Because the solution is a buffer, we will use the Henderson-Hasselbalch equation; thus

$$\text{pH} = \text{p}K_a + \log \frac{\text{mol A}^-}{\text{mol HA}}$$

$$3.20 = 3.036 + \log \frac{\text{mol A}^-}{\text{mol HA}}$$

This equation has two unknowns, so we need one additional equation, which is a mass balance on the weak acid and weak base. We know that their combined concentration is 0.100 mol/L and that we are making a solution of 0.750 L; thus, we have a total of 0.0750 mol of HA and of A^- , or that we have $0.0750 - x$ moles of HA where x is the moles of A^- . Substituting into the previous equation and solving

$$3.20 = 3.036 + \log \frac{x}{0.0750 - x}$$

$$0.164 = \log \frac{x}{0.0750 - x}$$

$$1.459 = \frac{x}{0.0750 - x}$$

$$0.1094 - 1.459x = x$$

gives $x = 0.0445$ mol A^- and $0.0750 - 0.0445 = 0.0305$ mol HA. The molar mass of tartrate is 188.2 g/mol and the molar mass of tartaric acid is 150.1 g/mol; thus, we need 8.37 g of $\text{KHC}_4\text{H}_4\text{O}_6$ and 4.58 g of $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$.

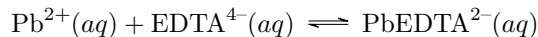
What is the pH of a 250 mL portion of this solution if it is mixed with 100.00 mL of 0.0200 M HCl, which mimics the pH and volume of stomach acid?

Answer. We are using one-third of the original buffer, which means we are using $0.0445/3 = 0.0148$ moles of A^- and $0.0305/3 = 0.0102$ moles of HA. Adding a strong acid converts some of the A^- to HA; thus

$$\text{pH} = 3.036 + \log \frac{0.0148 - (0.0200 \text{ M})(0.100 \text{ L})}{0.0102 + (0.0200 \text{ M})(0.100 \text{ L})} = 3.06$$

As expected, the pH becomes slightly more acidic than the solution's initial pH of 3.20.

Problem 6. The ligand EDTA forms strong metal-ligand complexes with most divalent metal ions. One of its important uses is to prevent a metal ion from precipitating as a hydroxide salt under basic conditions. Suppose you combine 0.0100 mol $\text{Pb}(\text{NO}_3)_2$ and 0.0500 mol of Na_4EDTA in a 1.00-L volumetric flask and dilute to volume using a pH 13.00 buffer. What is the concentration of uncomplexed Pb^{2+} in this solution given that the formation constant is 1.1×10^{18} for the reaction



Answer. Complexation equilibria often have very large equilibrium constants, which makes them challenging to work with as many calculators cannot handle the calculation to sufficient significant figures to give a meaningful answer; this is true, as well, when trying to solve more rigorously using, say, the quadratic equation. In this case, the standard approach to solving equilibrium problems typically results in finding that the $[\text{Pb}^{2+}]$ is 0, which is not possible. When working with complexation equilibria it always is easier to let the reaction go to completion and then come back to equilibrium, and to then make simplifying assumptions.

	$\text{Pb}^{2+}(\text{aq})$	$+$	$\text{EDTA}^{4-}(\text{aq})$	\rightleftharpoons	$\text{PbEDTA}^{2-}(\text{aq})$
initial	0.01		0.05		0
change	-0.01		-0.01		+0.01
new initial	0		0.04		0.01
change	$+x$		$+x$		$-x$
equilibrium	x		$0.04 + x$		$0.01 - x$

Substituting into the formation constant's equation and making the assumption that x is small gives

$$K = \frac{[\text{PbEDTA}^{2-}]}{[\text{Pb}^{2+}][\text{EDTA}^{4-}]} = \frac{0.01 - x}{(x)(0.04 + x)} = \frac{0.01}{(x)(0.04)} = 1.1 \times 10^{18}$$

Solving for x gives its value as 2.27×10^{-19} , which is the molar concentration of Pb^{2+} . The simplifying assumption here clearly introduces an error that is significantly smaller than 5%.

Given your result for the concentration of Pb^{2+} and knowing that the K_{sp} for $\text{Pb}(\text{OH})_2$ is 1.2×10^{-15} , is the amount of EDTA present sufficient to prevent the precipitation of $\text{Pb}(\text{OH})_2(s)$? Support your answer with one sentence explanation and a suitable calculation.

Answer. There are several ways to approach this, but all involve comparing the concentration of Pb^{2+} calculated above to that in equilibrium with $\text{Pb}(\text{OH})_2(s)$ in a pH 13.00 buffer. The concentration of OH^- in this buffer is 0.10 M, which means that the concentration of Pb^{2+} needed to precipitate $\text{Pb}(\text{OH})_2(s)$ is

$$K_{\text{sp}} = 1.2 \times 10^{-15} = [\text{Pb}^{2+}][\text{OH}^-]^2 = [\text{Pb}^{2+}](0.1)^2$$

Solving gives the concentration of Pb^{2+} as 1.2×10^{-13} ; as the actual concentration is much smaller, no precipitate will form.