

# Key for 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	10.8	12	4	16.0	21
2	11.4	13	5	15.2	21
3	9.2	12	6	15.8	21
Total					100

high score	scores 100–90	scores 89–80	scores $\leq 79$
97	2	7	11

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<sub>rxn</sub>  $\cdot$  K
- Faraday's constant ( $F$ ) is 96,485 C/mol e<sup>-</sup> or 96,485 J/V  $\cdot$  mol e<sup>-</sup>
- water's dissociation constant ( $K_w$ ) is  $1.00 \times 10^{-14}$

## !!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: Problems With Short Written Answers and/or With Short Calculations

**Problem 1.** Nitrogen dioxide,  $\text{NO}_2$ , is a reddish-brown gas and dinitrogen tetroxide,  $\text{N}_2\text{O}_4$ , is a colorless gas. The two gases form an equilibrium mixture defined by the reaction  $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$ . Suppose you have an equilibrium mixture of the two gases in a cylinder and note that the color of the mixture is a medium reddish-brown color. If you compress the gas by pushing down on the cylinder, will the gas mixture become a darker shade of reddish-brown or a lighter shade of reddish-brown, or will the color remain unchanged? In 2–3 sentences, explain this observation.

**Answer.** The equilibrium constant for this reaction is  $K = [\text{N}_2\text{O}_4]/[\text{NO}_2]^2$ . If we decrease the volume, then we increase the concentration of both gases by the same relative amount; however, as the concentration of  $\text{NO}_2$  is squared, the resulting value of  $Q$  is less than  $K$  and the system must shift to the right to move  $Q$  back to  $K$ . As a result, we have more  $\text{N}_2\text{O}_4$  and the color becomes lighter.

**Problem 2.** Equilibrium constants are temperature dependent. The value of  $K_w$ , for example, is  $1.0 \times 10^{-14}$  at  $25^\circ$  and is  $0.29 \times 10^{-14}$  at  $10^\circ$ . Based on this observation, is the dissociation of water exothermic or endothermic, or is there insufficient information to reach a conclusion. Limit your response to no more than 2–3 sentences.

**Answer.** The reaction that defines  $\text{p}K_w$  is  $2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$ . If the equilibrium constant decreases when the temperature drops to  $10^\circ$ , then the reaction must shift from the product-side to the reactant-side to generate thermal energy; thus, heat is a reactant for the reaction as written and the reaction is endothermic.

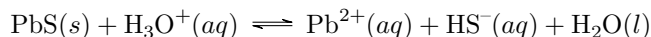
What is the pH of water at  $10^\circ$ ?

**Answer.** We know that  $\text{p}K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$  and that  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ ; thus,  $[\text{H}_3\text{O}^+] = \sqrt{0.29 \times 10^{-14}} = 5.39 \times 10^{-8}$ , or a pH of 7.27.

**Problem 3.** Many metals are found in nature as insoluble sulfide salts. Because sulfide is a weak base, the molar solubility of a metal sulfide depends on pH. Given the following information, write the reaction that controls the solubility of  $\text{PbS}$  in water at a fixed pH of 8.5, and report the value of its equilibrium constant.

$$K_{\text{sp,PbS}} = 8.0 \times 10^{-28} \quad K_{\text{a1,H}_2\text{S}} = 1.0 \times 10^{-7} \quad K_{\text{a2,H}_2\text{S}} = 1.3 \times 10^{-13}$$

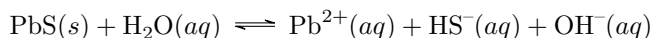
**Answer.** The two  $\text{p}K_a$  values for  $\text{H}_2\text{S}$  are 7.0 and 12.9, and they tell us that the only significant form of  $\text{H}_2\text{S}$  in solution is  $\text{HS}^-$  at a pH of 8.5. The solubility reaction for  $\text{PbS}$ , therefore, has  $\text{HS}^-$  as a product. We can accomplish this by adding together the solubility product reaction for  $\text{PbS}$ , which is  $\text{PbS}(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{S}^{2-}(aq)$ , and the inverse of the acid dissociation reaction for  $\text{HS}^-$ , which is  $\text{H}_3\text{O}^+(aq) + \text{S}^{2-} \rightleftharpoons \text{HS}^-(aq) + \text{H}_2\text{O}(l)$ , to obtain an overall reaction of



The equilibrium constant for this reaction is

$$K = K_{\text{sp}}/K_{\text{a2}} = (8.0 \times 10^{-28})/(1.3 \times 10^{-13}) = 6.2 \times 10^{-15}$$

The other option is to add together the solubility product reaction for  $\text{PbS}$  and the base dissociation reaction for  $\text{S}^{2-}$ , which is  $\text{S}^{2-} + \text{H}_2\text{O}(l) \rightleftharpoons \text{OH}^-(aq) + \text{HS}^-(aq)$ , to obtain an overall reaction of



The equilibrium constant for this reaction is

$$K = (K_{\text{sp}})K_{\text{b1}} = (K_{\text{sp}})(K_w)/K_{\text{a2}}(8.0 \times 10^{-28})(1.0 \times 10^{-14})/(1.3 \times 10^{-13}) = 6.2 \times 10^{-29}$$

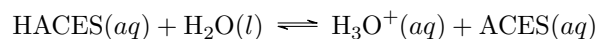
## Part B: Problems With More Involved Calculations

**Problem 4.** The weak acid N-(2-acetoamido)-2-aminoethanesulonic acid, which we abbreviate here as HACES, finds use in a variety of biological and biochemical research protocols, including the isoelectric focusing of proteins and SDS-PAGE separations. A publication by Interchim—a laboratory supply company that specializes in biological and biochemical reagents—notes that a 1.0 %w/v solution of HACES has a pH of 4.0 at 25°. Given this information, what is the  $pK_a$  for HACES? The molar mass for HACES is 182.2 g/mol.

**Answer.** The initial concentration of the weak acid,  $[\text{HACES}]_0$ , in mol/L is

$$[\text{HACES}]_0 = \frac{1.0 \text{ g}}{100 \text{ mL}} \times \frac{1 \text{ mol}}{182.2 \text{ g}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 0.0549 \text{ M}$$

The pH of 4.00 tells us that the equilibrium concentration of  $\text{H}_3\text{O}^+$  is  $1.0 \times 10^{-4} \text{ M}$ , which is the result of the weak acid's dissociation reaction



As we assume that the initial concentrations of ACES and  $\text{H}_3\text{O}^+$  are zero, we know that the equilibrium concentration of ACES is the same as that for  $\text{H}_3\text{O}^+$ , and that the equilibrium concentration of HACES is  $[\text{HACES}]_0 - [\text{H}_3\text{O}^+]$ . Substituting these concentrations into the equilibrium constant expression gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{ACES}]}{[\text{HACES}]} = \frac{[\text{H}_3\text{O}^+][\text{ACES}]}{[\text{HACES}]_0 - [\text{H}_3\text{O}^+]} = \frac{(1.0 \times 10^{-4})^2}{0.0549 - 1.0 \times 10^{-4}} = 1.82 \times 10^{-7}$$

or a  $pK_a$  of 6.74.

What is the  $pK_b$  for the conjugate weak base of HACES?

**Answer.** For a conjugate weak acid/weak base pair, we know that  $K_a \times K_b = K_w = 1.0 \times 10^{-14}$ , or that  $pK_a + pK_b = pK_w = 14.00$ . Given a  $pK_a$  of 6.74 for HACES, the  $pK_b$  for ACES is  $14.00 - 6.74 = 7.26$ .

**Problem 5.** The weak acid 2-(N-morpholino)ethanesulfonic acid monohydrate, which we abbreviate here as HMES, and its conjugate weak base, MES, are one of the so called “Good’s buffers” that find use in biological and biochemical protocols. Suppose you need to prepare 500.0 mL of a pH 7.00 HMES/MES buffer in which the total concentration of buffering agents is 0.100 M. The following reagents are available to you: a solution of 0.500 M HMES, a solution of 1.00 M HCl, and a solution of 1.00 M NaOH. Explain how you will prepare this buffer. The molar mass for HMES is 195.24 g/mol and its  $pK_a$  is 6.16.

*Answer.* We know that the combined moles of the buffer’s weak acid and its conjugate weak base is

$$[\text{HMES}] + [\text{MES}] = 0.100 \text{ M} \times 0.5000 \text{ L} = 0.0500 \text{ mol}$$

Given that the pH is more basic than the  $pK_a$  for HMES, we must prepare the buffer by starting with 0.0500 mol of HMES and sufficient NaOH to convert some HMES to MES. To obtain 0.0500 mol of HMES, we need

$$0.0500 \text{ mol HMES} \times \frac{1 \text{ L}}{0.500 \text{ mol HMES}} \times \frac{1000 \text{ mL}}{\text{L}} = 100.0 \text{ mL of } 0.500 \text{ M HMES}$$

To determine how much NaOH to add, we make use of the following form of the Henderson-Hasselbalch buffer equation

$$\text{pH} = pK_a + \log \frac{\text{mol MES}}{\text{mol HMES}} = pK_a + \log \frac{(\text{MES})_o + \text{mol NaOH}}{(\text{HMES})_o - \text{mol NaOH}}$$

the

Substituting in the desired pH of 7.00, the  $pK_a$  for HMES of 6.16, the initial moles of HMES of 0.0500, the initial moles of MES of 0, and setting moles of NaOH to  $x$  gives

$$7.00 = 6.16 + \log \frac{0 + x}{0.0500 - x}$$

$$0.84 = \log \frac{x}{0.0500 - x}$$

$$6.918 = \frac{x}{0.0500 - x}$$

$$0.3459 - 6.918x = x$$

$$0.3459 = 7.918x$$

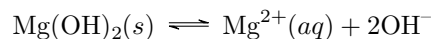
which we solve for  $x$ , obtaining 0.0437 moles of NaOH. This is equivalent to 43.7 mL of 1.0 M NaOH. Thus, to make the buffer we place 100.0 mL of 0.500 M HMES and 43.7 mL of 1.0 M NaOH in a 500-mL volumetric flask and dilute to volume with water.

Will your buffer have a greater capacity to neutralize strong acid or strong base? Justify your answer in 1–3 sentences.

*Answer.* A buffer exists for any pH that is within  $\pm 1$  of the  $pK_a$  for the buffer’s weak acid, which means a HMES/MES buffer exists for any pH between 5.16 and 7.16. Because our buffer’s pH of 7.00 is closer to its basic limit of 7.16 than its acidic limit of 5.16, it has more capacity to neutralize strong acid.

**Problem 6.** Sitting before you is a beaker that contains 500.0 mL of 0.300 M  $\text{Mg}(\text{NO}_3)_2$  and a weigh boat with 15.0 g of NaOH pellets. If you add the NaOH to the beaker, what are the concentrations of  $\text{Mg}^{2+}$  and of  $\text{OH}^-$  when equilibrium is established at 25°? The  $K_{\text{sp}}$  for  $\text{Mg}(\text{OH})_2$  is  $1.8 \times 10^{-11}$  at 25°. You may assume there is no change in volume when you add the NaOH to the solution.

**Answer.** Adding NaOH to a solution of  $\text{Mg}(\text{NO}_3)_2$  results in the precipitation of  $\text{Mg}(\text{OH})_2$ , which means the concentrations of  $\text{Mg}^{2+}$  and of  $\text{OH}^-$  at equilibrium depend on the solubility reaction



and its solubility product

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.8 \times 10^{-11}$$

There are several ways to solve the problem from this point, but the solution given here makes use of a simplifying assumption. To do this, we first let the precipitation reaction go to completion so that the changes in concentrations are small when it moves to equilibrium. The initial concentration of  $\text{Mg}^{2+}$  is 0.30 M and the initial concentration of  $\text{OH}^-$  is

$$\text{OH}^- = \frac{15.0 \text{ g NaOH}}{0.5000 \text{ L}} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} = 0.75 \text{ M}$$

The limiting reagent is  $\text{Mg}^{2+}$ , the reaction of which decreases the concentration of  $\text{OH}^-$  by  $2 \times 0.30$  from 0.75 M to 0.15 M; thus, the problem is equivalent to determining the concentrations of  $\text{Mg}^{2+}$  and of  $\text{OH}^-$  if we add solid  $\text{Mg}(\text{OH})_2$  to a solution that initially is 0.15 M in NaOH. If we define the concentration of  $\text{Mg}^{2+}$  at equilibrium as  $x$ , then the concentration of  $\text{OH}^-$  is  $0.15 + 2x$  and

$$1.8 \times 10^{-11} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (x)(0.15 + 2x)^2$$

If we assume that  $0.15 + 2x \approx 0.15$ , then we find that  $x$  is  $8 \times 10^{-11}$ . The simplifying assumption clearly is reasonable; thus, we find that  $[\text{Mg}^{2+}] = x = 8.0 \times 10^{-10}$  M and that  $[\text{OH}^-] = 0.15 + 2x \approx 0.15$  M.

Suppose that adding solid NaOH to the beaker increases slightly the volume. What effect does this have on the equilibrium concentrations for  $\text{Mg}^{2+}$  that you report above? Is your result too large or too small, or is your calculated result still correct? Justify your answer in 1–3 sentences.

**Answer.** One way to approach this is to assume that equilibrium is established without the increase in volume—which gives the results above—and then ask what happens if we dilute the solution by increasing the volume. If we dilute the solution, then the concentration of  $\text{OH}^-$ , which we calculated as 0.15 M, becomes slightly smaller. This, in turn, requires that the concentration of  $\text{Mg}^{2+}$  increase to maintain the  $K_{\text{sp}}$ ; thus, our calculation returns a concentration of  $\text{Mg}^{2+}$  that is too small.