Key for What Do We Remember?

The following set of questions draw on the coverage of equilibrium chemistry in Chem 260. Complete as many problems as you can in the time allotted. Do not work through the problems in order; instead, on your first pass through the problems, answer those problems for which you are most confident. When you complete your first pass through the problems, then continue making passes through the problems until you have answers to all problems or run out of time. The order in which you choose to work problems is important, so please make sure this is clear. You are free to ask questions of each other as you work.

Acid–Base Chemistry

1. Write the K_a reaction for acetic acid, CH_3COOH.

    The reaction is $CH_3COOH(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + CH_3COO^-(aq)$.

2. Knowing that K_a for acetic acid is 1.8×10^{-5}, what is K_b for the acetate ion, CH_3COO^-?

    For a weak acid and its conjugate weak base, the product of the weak acid's K_a and the weak base's K_b is equal to water's dissociation constant, K_w; thus

    $$K_b = \frac{K_w}{k_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

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3. What is the pH of a solution that is 0.10 M in acetic acid?

    To solve, we need to define the equilibrium concentrations of CH_3COOH, CH_3COO^-, and H_3O^+ in terms of a single variable, x. An ICE table is an easy way to accomplish this; thus

	$CH_3COOH(aq)$	+	$H_2O(l)$	$\rightleftarrows$	$H_3O^+(aq)$	+
initial	0.10		—		0	
change	$-x$		—		$+x$	
equilibrium	$0.1 - x$		—		x	

    Next, we substitute the equilibrium terms into the reaction's K_a expression and solve for x

    $$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{(x)(x)}{0.10 - x} = 1.8 \times 10^{-5}$$

    To solve we can rearrange this equation into the second-order polynomial equation

    $$x^2 + 1.8 \times 10^{-5}x - 1.8 \times 10^{-6} = 0$$

    and use the quadratic equation to find the two roots, one of which is chemically significant. Alternatively, we can simplify the problem by assuming that $0.10 - x \approx 0.10$, leaving us with

    $$\frac{(x)(x)}{0.10} = 1.8 \times 10^{-5} = 0$$

    Solving gives $x = 1.34 \times 10^{-3}$. As x is equal to the concentration of H_3O^+, the solution's pH is

    $$-\log[H_3O^+] = -\log(1.34 \times 10^{-3}) = 2.87$$

Before accepting this answer, we need to check our assumption. The error introduced by our assumption is

$$\frac{(0.1 - x) - (0.1)}{0.1} \times 100 = \frac{1.34 \times 10^{-3}}{0.10} \times 100 = 1.3\%$$

less than $\pm 5\%$; thus, we accept our simplifying assumption and the resulting pH of 2.87.

4. What is the pH of a solution that is 0.15 M in acetic acid and 0.075 M in acetate?

One approach to this problem is to use an ICE table. Alternatively, recognizing that this solution is a buffer because the ratio of the weak acid, CH_3COOH, and its conjugate weak base, CH_3COO^-, is greater than 0.10 but less than 10, we can assume that the equilibrium concentrations are, respectively, 0.15 M and 0.075 M and use the Henderson-Hasselbalch equation

$$pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]} = 4.74 + \log\frac{0.075}{0.15} = 4.44$$

Solubility–Precipiation Chemistry

5. The solubility of $PbCl_2$ is 0.695 g per 100.0 mL. What is the K_{sp} for $PbCl_2$?

The solubility reaction is $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ and the K_{sp} expression is

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

The equilibrium concentration of Pb^{2+} is equal to the molar solubility of $PbCl_2$; thus

$$[Pb^{2+}] = \frac{0.695 \text{ g } PbCl_2}{0.1000 \text{ L}} \times \frac{1 \text{ mol } PbCl_2}{278.1 \text{ g } PbCl_2} = 2.50 \times 10^{-2} \text{ M}$$

The equilibrium concentration of Cl^- is twice the equilibrium concentration of Pb^{2+}, or 5.00×10^{-2} M. The solubility product, therefore, is

$$K_{sp} = [Pb^{2+}][Cl^-]^2 = (2.50 \times 10^{-2})(5.00 \times 10^{-2} \text{ M})^2 = 6.25 \times 10^{-5}$$

6. What is the concentration of Ba^{2+} in a saturated solution of $Ba(IO_3)_2$? The solubility product for $Ba(IO_3)_2$ is 1.5×10^{-9}.

The solubility reaction is $Ba(IO_3)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2IO_3^-(aq)$ and the solubility product expression is

$$K_{sp} = [Ba^{2+}][IO_3^-]^2$$

At equilibrium, if the concentration of Ba^{2+} is x, then the concentration of IO_3^- is $2x$. Substituting into the solubility product expression and solving for x gives

$$K_{sp} = (x)(2x)^2 = 4x^3 = 1.5 \times 10^{-9}$$

its value as 7.2×10^{-4}; thus, the equilibrium concentration of Ba^{2+} is 7.2×10^{-4} M.

Complexation–Dissociation Chemistry

7. The reaction between Ca^{2+} and EDTA is $Ca^{2+}(aq) + Y^{4-}(aq) \leftrightarrows CaY^{2-}(aq)$, where Y^{4-} is the fully deprotonated form of EDTA. The equilibrium constant for this reaction is 4.90×10^{10}. What is the equilibrium concentration of Ca^{2+} if you mix together equal volumes of 0.20 M Ca^{2+} and 0.40 M Na_4Y?

   When we mix together the two solutions, the concentrations of Ca^{2+} and of Y^{4-} become 0.10 M and 0.20 M, respectively, as a result of their mutual dilution. When we work with a complexation reaction, it usually is simpler to convert the problem from one in which the complex forms into a problem in which the complex dissociates as this ensures that when we define the problem in terms of single variable, the value of that variable is reasonably small enough to allow for a simplifying assumption; the following ICE table accomplishes this

	$Ca^{2+}(aq)$	$+$	$Y^{4-}(aq)$	$\rightleftarrows$	$CaY^{2-}(aq)$
initial	0.10		0.20		0
react to completion	−0.10		−0.10		+0.10
new initial	0		0.10		0.10
change	$+x$		$+x$		$-x$
equilibrium	x		$0.10 + x$		$0.10 - x$

   Substituting the last row into the formation constant expression gives

   $$K_f = \frac{[CaY^{2-}]}{[Ca^{2+}][Y^{4-}]} = \frac{0.10 - x}{(x)(0.10 + x)} = 4.90 \times 10^{10}$$

   To simplify the prolem, we make the following two assumptions

   $$0.1 - x \approx 0.1 \text{ and } 0.1 + x \approx 0.1$$

   and solve for x

   $$K_f = \frac{0.10}{(x)(0.10)} = 4.90 \times 10^{10}$$

   obtaining a value of 2.04×10^{-11} for x; thus, the equilibrium concentration of Ca^{2+} is 2.04×10^{-11} M.

Oxidation–Reduction Chemistry

8. For an oxidation–reduction reaction, what are the relationships between the reaction's equilibrium constant and its free energy, between its oxidation–reduction potential and its free energy, and between its redox potential and its equilibrium constant?

   The three relationships are, in order

   $$\Delta G^o = -RT \ln K$$

   $$\Delta G^o = -nFE^o$$

   $$E^o = \frac{RT}{nF} \ln K$$