Equlibrium Practice Exam Key

Note: All problems included in this practice exam are drawn from problems used in previous semesters. Exams typically include 7 or 8 problems that are a mixture of qualitative problems calling for written explanations and quantitative problems that involve calculations and, in some cases, written explanations.

On the following pages are problems covering material in equilibrium chemistry. 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		12	5		16
2		12	6		20
3		12	7		16
4		12	Total		100

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 • °C
- the gas constant (R) is 8.314 J/mol$_{\text{rxn}}$ • K
- Faraday's constant (F) is 96,485 J/V • mol e$^-$
- water's dissociation constant (K_w) is 1.00×10^{-14}

Problem 1. When you ingest a drug, it is absorbed into the bloodstream in either the stomach, the intestines, or both the stomach and the intestines. For a drug that is a weak acid or a weak base, absorption happens when the compound is in its neutral, unionized form. Quinidine, $C_{20}H_{24}N_2O_2$, is used to treat arrhythmia; it is a weak base with a K_b of 3.63×10^{-6} at body temperature. Knowing that the pH of stomach fluid is approximately 2 and that the pH of intestinal fluid is approximately 8, is quinidine absorbed in the stomach, in the intestines, or in both? Explain the reason for your decision in no more than three sentences.

Quinidine will absorb in the intestines. The pK_b *for quinidine, Q, is 5.44, which means the p*K_a *for its conjugate weak acid,* QH^+*, is 8.56. At a pH of less than 7.56, the only significant form of the compound is* QH^+*; thus, absorption will occur only when the pH is greater than 7.56, which means quinidine is absorbed in the intestines only.*

Problem 2. To investigate an equilibrium reaction between the gases A, B, and C, you fill a 0.500-L flask with 0.800 mol A, 0.400 mol B, and 0.100 mol C and allow the system to reach equilibrium. Once equilibrium is reached, you find that the flask contains 0.500 mol A, 0.300 mol B, and 0.300 mol C. Using this information, determine (a) the reaction's stoichiometry and (b) the reaction's equilibrium constant.

*To determine the reaction's stoichiometry we need to find the relative change in the moles of A, B, and C as the reaction moves to equilibrium; thus, Δmol A = 0.500 mol A – 0.800 mol A = –0.300 mol A; Δmol B = 0.300 mol B – 0.400 mol B = –0.100 mol B; Δmol C = 0.300 mol C – 0.100 mol C = +0.200 mol C. Based on these results, three moles of A and one mole of B react to form two moles of C, or

$$3A(g) + B(g) \rightleftharpoons 2C(g)$$

To find the equilibrium constant, we substitute the equilibrium concentrations into the reaction's equilibrium constant expression

$$K = \frac{[C]^2}{[A]^3[B]} = \frac{\left(\frac{0.300\ mol\ C}{0.500\ L}\right)^2}{\left(\frac{0.500\ mol\ A}{0.500\ L}\right)^3\left(\frac{0.300\ mol\ B}{0.500\ L}\right)} = 0.600$$

*

Problem 3. The decomposition of ammonium chloride into ammonia and hydrogen chloride

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

is endothermic with an equilibrium constant of 0.0167 at 500 K. Will the reaction's equilibrium constant increase, decrease, or remain the same if you increase the temperature to 1000 K? Explain your decision in no more than three sentences.

For an endothermic reaction we can view heat as a reactant. From Le Châtelier's Principle, increasing the temperature is equivalent to adding heat, which shifts the reaction to the right and increases the concentrations of NH_3 *and HCl; thus, the value of the equilibrium constant increases.*

A 1.00–L flask is filled with 0.0500 mol each of $NH_3(g)$, $HCl(g)$, and $NH_4Cl(s)$ and heated to 500 K. Will the moles of NH_4Cl in the flask increase, decrease, or remain the same? Explain the reason for your decision in no more than three sentences.

For the initial condition, we have $Q = [NH_3][HCl] = (0.0500)(0.0500) = 0.00250$*, which is smaller than the equilibrium constant of 0.0167. With* $Q < K$*, the reaction must shift to the right to reach equilibrium, decreasing the mass of* NH_4Cl*.*

Problem 4. Adding a dilute solution of NaSCN to a suspension of the white solid AgCl produces an amber precipitate of AgSCN. Which of these two solids—AgCl or AgSCN—has the smallest K_{sp}? Explain your decision in no more than three sentences.

Because the equilibrium AgCl(s) + SCN⁻(aq) $\rightleftharpoons$ AgSCN(s) + Cl⁻(aq) lies to the right, we know AgSCN is less soluble than AgCl and has the smaller of the two K_{sp} *values. Another approach is to note that the equilibrium constant for this reaction is* $\frac{K_{sp,AgCl}}{K_{sp,AgSCN}} > 1$*, which means* $K_{sp,SCN}$ *is smaller than* $K_{sp,AgCl}$.

A saturated solution of $Fe(OH)_3$ has a lower pH than a saturated solution of $Al(OH)_3$. Which of these two solids—$Fe(OH)_3$ or $Al(OH)_3$—has the greater molar solubility? Explain your decision in no more than three sentences.

The solubility reaction for both compounds produces three moles of hydroxide for each mole of metal hydroxide that dissolves; thus, the compound that produces the greatest [OH⁻] has the greatest molar solubility. As the saturated solution of $Al(OH)_3$ *is more basic, it has the greatest [OH⁻], making* $Al(OH)_3$ *the compound with the greater molar solubility.*

Problem 5. Many household bleaches are dilute solutions of sodium hypochlorite, NaOCl. For example, the bleach in my laundry room states that it contains 5.5 g NaOCl per 0.100 L. What is the pH of this solution? The K_a for HOCl is 3.0×10^{-8}.

The initial concentration of OCl⁻ is

$$\frac{5.5\ g\ NaOCl}{0.100\ L} \times \frac{1\ mol\ NaOCl}{74.44\ g\ NaOCl} \times \frac{1\ mol\ OCl^-}{1\ mol\ NaOCl} = 0.739\ M$$

Using an ICE table (not shown) for the weak base's dissociation reaction

$$OCl^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HOCl(aq)$$

the equilibrium concentrations of OCl⁻, OH⁻, and HOCl are, respectively, 0.739 – x, x, and x. Substituting into the K_b *expression gives*

$$K_b = \frac{[OH^-][HOCl]}{[OCl^-]} = \frac{(x)(x)}{0.739 - x} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{3.0 \times 10^{-8}} = 3.33 \times 10^{-7}$$

Because K_b *is small, we will assume that* $0.739 - x \approx 0.739$ *and solve for x; thus*

$$\frac{(x)(x)}{0.739} = 3.33 \times 10^{-7}$$

This gives x as 4.96×10^{-4}*. The error introduced in the assumption* $0.739 - x \approx 0.739$ *is*

$$100 \times \frac{4.96 \times 10^{-4}}{0.739} = 0.067\%$$

which is negligible; thus, the concentration of OH⁻ is 4.96×10^{-4} *M, the pOH is* $-log(4.96 \times 10^{-4})$ *or 3.30, and the pH is 14 – 3.30 = 10.70.*

Problem 6. A biochemist wishes to use X-ray diffraction to determine the structure of a crystalline protein. To isolate crystals of the protein, she needs a buffer with a pH of 5.20. How many grams of sodium acetate, CH_3COONa, does she need to add to 2.00-L of 0.500 M acetic acid, CH_3COOH, to prepare this buffer. The pK_a for acetic acid is 4.757.

Using the buffer equation we solve for the moles of CH_3COO^- in terms of the moles of CH_3COO^- and the grams of CH_3COONa; thus

$$5.20 = 4.757 + log \frac{mol\ CH_3COO^-}{mol\ CH_3COOH}$$

which we solve to give a mole ratio of 2.773. Now we can find the g of sodium acetate.

$$mol\ CH_3COO^- = 2.773 \times mol\ CH_3COOH = 2.773 \times 0.500\ M \times 2.00\ L = 2.773\ mol$$

$$2.773\ mol\ CH_3COO^- \times \frac{1\ mol\ CH_3COONa}{1\ mol\ CH_3COO^-} \times \frac{82.03\ g\ CH_3COONa}{mol\ CH_3COONa} = 227\ g\ CH_3COONa$$

Does this buffer have a greater capacity to neutralize strong acid or strong base? Explain your decision in no more than three sentences.

Because the buffer has more of its conjugate weak base than its conjugate weak acid (2.773× more, in fact), it has more capacity to neutralize strong acid than it has capacity to neutralize strong base.

What is the pH if you add 5.00 mL of 6.00 M NaOH to one-half of this buffer?

When we add a strong base to the buffer, we convert some of the buffer's weak acid form into its conjugate weak base form, with the amount determined by the moles of strong base added. Here we are using half of the buffer (1.00 L) so we have 0.500 M × 1.00 L, or 0.500 mol CH_3COOH and we have 2.773 mol × 0.500, or 1.3865 mol CH_3COO^-. Adding 5.00 mL of 6.00 M NaOH is equivalent to adding 6.00 M × 0.00500 L, or 0.0300 mol OH^-. Using the buffer equation, we find that the pH is

$$pH = 4.757 + log \frac{mol\ CH_3COO^- + mol\ OH^-}{mol\ CH_3COOH - mol\ OH^-} = 4.757 + log \frac{1.3865 + 0.0300}{0.500 - 0.0300} = 5.23$$

How many mL of 6.00 M HCl can the other half of this buffer neutralize before the pH falls below 5.00?

When we add a strong acid to the buffer, we convert some of the buffer's weak base form into its conjugate weak acid form, with the amount determined by the moles of strong acid added. Here we are using half of the buffer (1.00 L) so we have 0.500 M × 1.00 L = 0.500 mol CH_3COOH and we have 2.773 × 0.500 = 1.3865 mol CH_3COO^-. Using the buffer equation, the moles of strong acid we can add is

$$5.00 = 4.757 + log \frac{mol\ CH_3COO^- - mol\ HCl}{mol\ CH_3COOH + mol\ HCl} = 4.757 + log \frac{1.3865 - mol\ HCl}{0.500 + mol\ HCl}$$

$$\frac{1.3865 - mol\ HCl}{0.500 + mol\ HCl} = 1.750$$

which is 0.186 mol HCl, or

$$0.186\ mol\ HCl \times \frac{1.00\ L}{6.00\ M\ HCl} \times \frac{1000\ mL}{L} = 31.0\ mL$$

Problem 7. Some progressive hair coloring products, such as Grecian Formula 16, contain soluble lead acetate, $Pb(CH_3CO_2)_2$. When rubbed into hair, Pb^{2+} reacts with the sulfur in hair proteins to form insoluble lead sulfide, PbS, which is black in color. A typical application of Grecian Formula 16 forms approximately 1.3 mg of PbS. At the pH of a typical shampoo, the solubility of PbS is controlled by the reaction

$$\mathrm{PbS}(s) + 2\mathrm{H_3O^+}(aq) \rightleftharpoons \mathrm{Pb^{2+}}(aq) + \mathrm{H_2S}(aq) + 2\mathrm{H_2O}(l)$$

for which the equilibrium constant is 3.0×10^{-7}. Suppose someone who uses Grecian Formula 16 washes his or her hair using 12.0 L of water and shampoo at a constant pH of 5.5. How many mg of PbS are lost during this process?

Using an ICE table (not shown), we expect an equilibrium concentration of x for Pb^{2+} and for H_2S, and an equilibrium concentration of 3.16×10^{-6} M H_3O^+ (because the concentration of H_3O^+ is fixed to a constant pH). Substituting into the equilibrium constant expression

$$K = \frac{[Pb^{2+}][H_2S]}{[H_3O^+]^2} = \frac{x^2}{(3.16 \times 10^{-6})^2} = 3.0 \times 10^{-7}$$

and solving for x gives its value as 1.73×10^{-9} M. This is the molar concentration of Pb^{2+} and, therefore, the molar solubility of PbS. The mg of PbS dissolved in solution are

$$\frac{1.73 \times 10^{-9} \ mol\ PbS}{L} \times 12.0 \ L \times \frac{239.3 \ g\ PbS}{mol} \times \frac{1000 \ mg}{g} = 0.00497 \ mg\ PbS$$