Chem 260 – Second Exam Key

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 one question, then move on to another question; working on a new question may suggest an approach to the one 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.

Be sure to clearly state and verify any assumptions you make when solving an equilibrium problem.

Problem 1_____/10 Problem 2_____/10 Problem 3_____/10 Problem 4 _____/10

Problem 5_____/17 Problem 6_____/17 Problem 7_____/26

Total__________

A few constants are given here:

d_{H_2O} = 1.00 g/mL S_{H_2O} = 4.184 J/g•oC

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

$K_w = 1.00\times10^{-14}$

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? Circle your choice and explain the reason for your decision in no more than three sentences.

the stomach only **the intestines only** both the stomach and intestines

The pK_b for quinidine, Q, is 5.44, which means the pK_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

$$\Delta\text{mol A} = \text{final mol A} - \text{initial mol A} = 0.500 \text{ mol A} - 0.800 \text{ mol A} = -0.300 \text{ mol A}$$

$$\Delta\text{mol B} = 0.300 \text{ mol B} - 0.400 \text{ mol B} = -0.100 \text{ mol B}$$

$$\Delta\text{mol C} = 0.300 \text{ mol C} - 0.100 \text{ mol C} = +0.200 \text{ mol C}$$

Based on these results, three moles of A and one mole of B react to form two moles of C, or

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

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

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

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

$$\text{heat} + NH_4Cl(s) \leftrightarrows NH_3(g) + HCl(g)$$

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? Circle your choice and explain the reason for your decision in no more than two sentences.

the equilibrium constant will: **increase** decrease remain the same

As shown above, 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, increases the concentrations of NH_3 and HCl, and inceases the value of the equilibrium constant.

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 mass of NH_4Cl increase, decrease, or remain the same? Circle your choice and explain the reason for your decision in no more than two sentences.

the mass of NH_4Cl will: increase **decrease** remain the same

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.

A 1.00–L flask containing $NH_3(g)$, $HCl(g)$, and $NH_4Cl(s)$ is at equilibrium. Will the concentration of NH_3 increase, decrease, or remain the same if additional NH_4Cl is added? Circle your choice and explain the reason for your decision in no more than two sentences.

the mass of NH_3 will: increase decrease **remain the same**

Because NH_4Cl is a solid, it does not appear in the equilibrium constant expression. Increasing its mass, therefore, has no effect on the position of the equilibrium.

Problem 4. When the soluble salt BHY(s) dissolves in water, it forms a slightly basic solution of $BH^+(aq)$ and $Y^-(aq)$. Knowing that the pK_a for BH^+ is 5.00, is the pK_a for the weak acid HY greater than 5.00, less than 5.00, or equal to 5.00? Circle your choice and explain the reason for your decision in no more than three sentences.

the pK_a for HY is: **greater than 5.00** less than 5.00 equal to 5.00

If a solution that contains the weak acid BH^+ and the weak base Y^- is slightly basic, then Y^- is a stronger weak base than BH^+ is as a weak acid. Because stronger bases have weaker conjugate acids, we know that HY is a weaker acid than BH^+; thus, the pK_a for HY is greater than 5.00.

Problem 5. Barbituric acid, $HC_4H_5N_2O_3$, which we abbreviate as HB, was discovered by Adolph von Baeyer and named for Saint Barbara, on whose feast day the discovery occurred. Knowing that a solution that contains 1.6 g of HB per 0.250 L has a pH of 2.66, what is the K_a for HB?

The initial concentration of HB is

$$\frac{1.6 \text{ g HB}}{0.250 \text{ L}} \times \frac{1 \text{ mol HB}}{130.10 \text{ g HB}} = 0.0492 \text{ M}$$

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

$$HB(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$$

the equilibrium concentrations of HB, H_3O^+, and A^- are, respectively, $0.0492 - x$, x, and x. Because we know the equilibrium pH is 2.66, we know that $[H_3O^+] = x = 2.188 \times 10^{-3}$; thus

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(x)(x)}{0.0492 - x} = \frac{(2.188 \times 10^{-3})^2}{0.0492 - 2.188 \times 10^{-3}} = 1.02 \times 10^{-4}$$

Problem 6. 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

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

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

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

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

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

which gives x as 4.96×10^{-4}. The error introduced in making the assumption $0.739 - x \approx 0.739$ is $100 \times (4.96 \times 10^{-4}/0.739)$, or 0.067%, is negligible; thus, the $[OH^-]$ is 4.96×10^{-4} M, which is a pOH of 3.30 and a pH of 10.70.

Problem 7. 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 H-H equation we solve for the moles of CH_3COO^- in terms of the moles of CH_3COO^- and the grams of CH_3COONa; thus

$$5.20 = 4.757 + \log \frac{\text{mol CH}_3\text{COO}^-}{\text{mol CH}_3\text{COOH}}$$

$$\text{mol CH}_3\text{COO}^- = 2.773 \times \text{mol CH}_3\text{COOH} = 2.773 \times 0.500 \text{ M} \times 2.00 \text{ L} = 2.773 \text{ mol}$$

$$2.773 \text{ mol CH}_3\text{COO}^- \times \frac{1 \text{ mol CH}_3\text{COONa}}{1 \text{ mol CH}_3\text{COO}^-} \times \frac{82.03 \text{ g CH}_3\text{COONa}}{\text{mol CH}_3\text{COONa}} = 227 \text{ g CH}_3\text{COONa}$$

Does this buffer have a greater capacity to neutralize strong acid or strong base? Circle your choice and explain the reason for your decision in no more than two sentences.

the buffer capacity is greatest against: **a strong acid** a strong base

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 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 = 0.500 mol CH_3COOH and we have 2.773×0.500 = 1.3865 mol CH_3COO^-. Adding 5.00 mL of 6.00 M NaOH is 6.00 M×0.00500 L, or 0.0300 mol OH^-. From the H-H equation we find that the pH is

$$\text{pH} = 4.757 + \log \frac{\text{mol CH}_3\text{COO}^- + \text{mol OH}^-}{\text{mol CH}_3\text{COOH} - \text{mol OH}^-} = 4.757 + \log \frac{1.3865 + 0.0300}{0.500 - 0.300} = 5.24$$

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 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^-. From the H-H equation we find that the moles of strong acid we can add is

$$5.00 = 4.757 + \log \frac{\text{mol CH}_3\text{COO}^- - \text{mol HCl}}{\text{mol CH}_3\text{COOH} + \text{mol HCl}} = 4.757 + \log \frac{1.3865 - \text{mol HCl}}{0.500 + \text{mol HCl}}$$

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

which is 0.186 mol HCl 0.186, or

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