Chem 260 – Second Exam

On the following pages are six problems covering material in equilibrium chemistry. Read each problem carefully and think about how best to approach the problem before you begin work. If you aren't sure how to begin a problem, then move on; working on a new problem may stimulate an idea that helps you solve the more troublesome one. For problems requiring a written response, be sure that your answer directly and clearly answers the question. No brain dumps allowed! Generous partial credit is available, but only if you include sufficient work for evaluation.

Problem 1 _____/14	Problem 4 _____/18
Problem 2 _____/14	Problem 5 _____/18
Problem 3 _____/18	Problem 6 _____/18

Total__________

A few constants are given here:

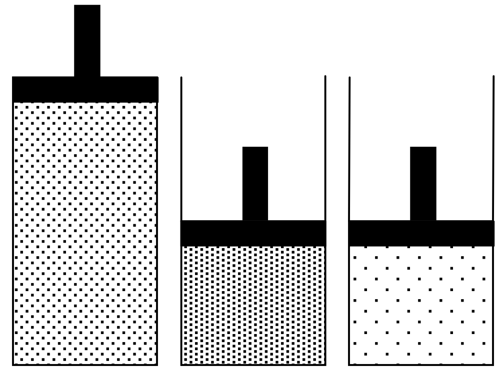
$d_{H_2O} = 1.00$ g/mL $S_{H_2O} = 4.184$ J/g·°C

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

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

and some equilibrium constants here:

acid	K_{a1}	K_{a2}	K_{a3}
NH_4^+; ammonium	5.6×10^{-10}		
HF; hydrofluoric acid	7.2×10^{-4}		
HN_3; azoic acid	1.9×10^{-5}		
H_3PO_4; phosphoric acid	7.5×10^{-3}	6.2×10^{-8}	4.8×10^{-13}



Problem 1. Shown to the right is a cylinder containing a mixture of NO_2, which is a reddish-colored gas, and N_2O_4, which is a colorless gas. The cylinder on the left shows the system's initial equilibrium due to the reaction:

$$2NO_2(g) \leftrightarrows N_2O_4(g)$$

Note that the black part is a piston and that the shading represents the color of the gas mixture (the denser the dots, the darker the color). The middle cylinder shows the system immediately after compressing the gases and the cylinder on the right shows the system after it establishes its new equilibrium position. In two or three concise, but well-written sentences, use equilibrium theory to explain the differences in the color of the gas mixtures in the three cylinders.

Answer. Pushing down on the piston compresses the gases into a smaller volume, increasing the concentrations of both gases; thus, the darker color due to the greater concentration of NO_2. According to Le Châtelier's principle, upon a decrease in volume a reaction shifts in the direction of the fewest species. Thus, the reaction shifts to the right and the concentration of NO_2 decreases.

When a flask containing an equilibrium mixture of NO_2 and N_2O_4 is cooled, the color of the gas becomes lighter. What conclusion can you reach about ΔH^o based on this observation. Explain your answer in one or two concise, but well-written sentences.

Answer. When temperature decreases a reaction shifts in the direction that releases energy. Since the reaction shifts to the right in this case, heat is a product and the reaction is exothermic.

Problem 2. Dave Roberts has prepared equimolar solutions for the Chem 130 lab of the following compounds: HCl, NaOH, NH_4Cl, HF, NH_3, KNO_3 and NaF. Being in a mischievous mood, one of his storeroom helpers relabeled the solutions as A, B, C, D, E, F and G. Rather than preparing the solutions again, Dave used pH paper to determine whether each solution was acidic, basic or neutral. He also measured the conductivity of each solution, knowing that a "high" value means that the solution has lots of dissolved ions. The results are shown here:

test	A	B	C	D	E	F	G
pH	basic	acidic	basic	acidic	acidic	basic	neutral
conductivity	high	high	low	high	low	high	high
identity	**NaOH**	**NH_4Cl**	**NH_3**	**HCl**	**HF**	**NaF**	**KNO_3**

This information was not quite enough to determine the identity of all seven solutions. When Dave mixed equal volumes of solutions A and B and determined that the resulting solution was basic, he had enough information to correctly label each solution. Complete the table by filling in the identity of each solution. No written explanation is required, but you are welcome to include one here (or on the reverse side of this page):

Explanation. The key to solving this problem is to classify the compounds in terms of their acidity and their conductivity; thus

compound	HCl	NaOH	NH_4Cl	HF	NH_3	KNO_3	NaF
pH	acidic	basic	acidic	acidic	basic	neutral	basic
conductivity	high	high	high	low	low	high	high

From this we can see that HF must be solution E, NH_3 must be solution C and KNO_3 must be solution G. We know, as well, that solution A must be NaOH or NaF and that solution B must be HCl or NH_4Cl. Mixing together NaOH and HCl gives a neutral solution, so these cannot be solutions A and B. Mixing together NaOH and NH_4Cl will give a solution of NH_3, which is basic; thus A is NaOH and B is NH_4Cl. This leaves NaF as solution F and HCl as solution D.

Problem 3. Those of you who have completed Chem 130 may recall that solutions of many transition metal ions are acidic. For example, the pH of 0.100 M $Fe(NO_3)_3$ is 1.66 due to the following equilibrium reaction:

$$Fe(H_2O)_6^{3+} + H_2O \leftrightarrows H_3O^+ + Fe(H_2O)_5(OH)^{2+}$$

What is the value of K_a for $Fe(H_2O)_6^{3+}$?

Answer. A pH of 1.66 corresponds to an equilibrium $[H_3O^+]$ of 2.19×10^{-2} M. An ICE table helps organize our approach to the problem (with entries in **bold** provided):

$Fe(H_2O)_6^{3+}$	+	H_2O	$\leftrightarrows$	H_3O^+	+	$Fe(H_2O)_5(OH)^{2+}$
0.100		-		**0**		**0**
$-\ 2.19\times10^{-2}$		-		$+\ 2.19\times10^{-2}$		$+\ 2.19\times10^{-2}$
7.81×10^{-2}		-		$\mathbf{2.19\times10^{-2}}$		2.19×10^{-2}

Substituting into the equilibrium constant expression gives

$$K_a = \frac{(2.19\times10^{-2})(2.19\times10^{-2})}{(7.81\times10^{-2})} = 6.14\times10^{-3}$$

Problem 4. Sodium azide, NaN_3, sometimes is used to prevent bacteria from growing in biological media. For example, one set of directions for preparing samples for the detection of recombinant proteins makes use of a stock solution containing 2.0 g of NaN_3 in 20.0 mL of water. What is the pH of a solution prepared by diluting 10.0 mL of this stock solution to 100.0 mL?

Answer. A solution of NaN_3 will be basic because N_3^- is a weak base. Begin by finding the concentration of N_3^- in the final solution; thus

$$\frac{2.0\text{ g}}{0.020\text{ L}} \times \frac{1\text{ mol}}{65.02\text{ g}} \times \frac{10\text{ mL}}{100\text{ mL}} = 0.154\text{ M}$$

Using an ICE table to help organize information and solving gives

N_3^-	+	H_2O	$\leftrightarrows$	OH^-	+	HN_3
0.154		-		0		0
- X		-		+ X		+ X
0.154 – X		-		X		X

$$\frac{X^2}{0.154 - X} \approx \frac{X^2}{0.154} = \frac{K_w}{K_{a,HN_3}} = \frac{1.00\times10^{-14}}{1.9\times10^{-5}} = 5.26\times10^{-10}$$

Solving gives X as 9.00×10^{-6}, which is the concentration of OH^-. This gives the pOH as 5.05 and the pH as 8.95. Note that the simplifying assumption is acceptable, giving an error of 5.8×10^{-3} %.

Problem 5. A common buffer used in biochemistry is phosphate buffered saline (PBS). One recipe for a PBS buffer is given as follows: transfer 10.9 grams of Na_2HPO_4, 3.2 g of NaH_2PO_4 and 90 g of NaCl (saline) to a 1-L volumetric flask and dilute to volume. What is the expected pH of this buffer?

Answer. This solution is a $H_2PO_4^-/HPO_4^{2-}$ buffer. Note that NaCl has no effect on pH and can be ignored. The moles of the weak acid and weak base are, respectively

$$3.2 \text{ g NaH}_2\text{PO}_4 \times \frac{1 \text{ mol}}{120 \text{ g}} = 2.667 \times 10^{-2} \text{ mol H}_2\text{PO}_4^-$$

$$10.0 \text{ g Na}_2\text{HPO}_4 \times \frac{1 \text{ mol}}{142 \text{ g}} = 7.676 \times 10^{-2} \text{ mol HPO}_4^{2-}$$

Because the solution is a buffer, we can simplify our approach to the problem by using the Henderson-Hasselbach equation; thus

$$\text{pH} = \text{pK}_a + \log\frac{\text{mol HPO}_4^{2-}}{\text{mol H}_2\text{PO}_4^-} = 7.208 + \log\frac{7.676\times10^{-2}}{2.667\times10^{-2}} = 7.67$$

Problem 6. Suppose that you need the actual pH of the buffer in Problem 5 to be 0.50 pH units less than the value you calculated. How many mL of 6.0 M HCl do you need to add to accomplish this?

Answer. Adding a strong acid converts some of the HPO_4^{2-} to $H_2PO_4^-$. Because the solution will still be a buffer, we again can use the Henderson-Hasselbach equation to simply our approach; thus

$$7.17 = 7.208 + \log\frac{7.676\times10^{-2} - \text{mol HCl}}{2.667\times10^{-2} + \text{mol HCl}}$$

Solving gives the moles of HCl as 0.02135. Converting to mL of HCl gives

$$\frac{0.02135 \text{ mol HCl}}{6 \text{ mol HCl/L}} \times \frac{1000 \text{ mL}}{\text{L}} = 4.55 \text{ mL of } 6.0 \text{ MHCl}$$