CHEM 1002 A and V Midterm Test #2
March 3, 2017

Part A. Answer each of the six questions with a few sentences or equations where necessary. (5 Marks each)

1. For the exothermic reaction $HClO_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + ClO^-_{(aq)}$ initially at equilibrium, which direction will the reaction shift (left, right or no shift) if we make the following changes? (Tick one box in each case.)

Change	Left	Right	No Shift	Reason
Add some $H_2O_{(l)}$		✓		Although $[H_2O_{(l)}]$ is not included in Q, diluting the solution will cause $[H_3O^+][ClO^-]$ to decrease faster than [HClO]
Add some $HNO_{3(aq)}$	✓			Adding $HNO_{3(aq)}$ will increase $[H_3O^+]$. The reaction will shift left to decrease it
Warm the solution	✓			Reactions shift in the endothermic direction when warmed
Add some $NaOH_{(s)}$		✓		Adding $NaOH_{(aq)}$ will decrease $[H_3O^+]$. The reaction will shift right to increase it
Increase the pressure			✓	All species are in solution. Pressure has no effect on the position of the equilibrium

2. For $H_2SO_{4(aq)}$, $K_{a_2} < K_{a_1}$ Show the relevant reactions and explain why this is so.

$$H_2SO_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HSO^-_{4(aq)}$$
$$HSO^-_{4(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + SO^{2-}_{4(aq)}$$

In the first reaction, a proton is being separated from a singly charge $HSO_4^-{}_{(aq)}$ ion. In the second, another proton is being separated from a doubly charge $SO_4^{2-}{}_{(aq)}$ ion. This greater charge requires more energy to separate the ions, thus K_{a2} is smaller.

3. What is the conjugate base of $OH^-_{(aq)}$?

$O^{2-}_{(aq)}$

4. How is it possible to make a buffered solution from $NaOH_{(aq)}$ and $HF_{(aq)}$? Show the relevant reaction and explain.

Adding $NaOH_{(aq)}$ to $HF_{(aq)}$ causes the reaction $OH^-_{(aq)} + HF_{(aq)} \rightarrow F^-_{(aq)} + H_2O_{(l)}$. As long as not too much $OH^-_{(aq)}$ is added, there will be some $HF_{(aq)}$ and some $F^-_{(aq)}$ in the solution, which collectively make a buffer.

5. Would the solubility of $Na_2S_{(s)}$ increase or decrease as the pH is decreased? Show the relevant reactions and explain. $K_{a2}(H_2S_{(aq)}) = 9.1 \times 10^{-8}$; $K_b(NaOH_{(aq)}) = \infty$.

The salt dissolves according to $Na_2S_{(s)} \rightarrow 2Na^+_{(aq)} + S^{2-}_{(aq)}$
The $Na^+_{(aq)}$ ion is a very weak acid since $NaOH_{(aq)}$ is a very strong base. Thus this ion has no effect on solution pH. But the $S^{2-}_{(aq)}$ ion is basic because its conjugate acid, $HS^-_{(aq)}$, is a weak acid. Therefore:
$S^{2-}_{(aq)} + H_2O_{(l)} \rightleftharpoons HS^-_{(aq)} + OH^-_{(aq)}$
Decreasing the pH decreases $[OH^-_{(aq)}]$. This causes this last equilibrium to shift right, $[S^{2-}_{(aq)}]$ to decrease, and so more $Na_2S_{(s)}$ dissolves to replace it. The solubility therefore increases.

6. Explain why 2,2-dichloropropanoic acid is a stronger acid than 3,3-dichloropropanoic acid.

The two Cl atoms on carbon number 2 are closer to the acidic hydrogen than the two on carbon number 3. They have a greater attraction of the O-H bond electrons, weakening it, and causing the acid to be stronger.

Part B. **Answer any three of B1, B2, B3 and B4. If you answer all four, the best three will count. (20 marks each)**

B1. The reaction 2 $NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ has K = 3.09 at 25.0°C. 2.00 bar of $N_2O_{4(g)}$ is sealed in a vessel at 25.0°C. Find the equilibrium partial pressures (in bar) of both gases.

	$NO_{2(g)}$	**$N_2O_{4(g)}$**
Initial, bar	0	2.00
Change, bar	+2x	-x
Equilibrium, bar	2x	2.00-x

At equilibrium,

$$K = \frac{p_{N_2O_4}}{p^2_{NO_2}} = \frac{2.00 - x}{(2x)^2}$$

$$3.09(2x)^2 = 2.00 - x$$

$$12.36x^2 + x - 2.00 = 0$$

$$x = \frac{-1 \pm \sqrt{1^2 - 4(12.36)(1)}}{2(12.36)} = 0.364 \text{ or } -0.445$$

The negative root is physically meaningless, thus x = 0.364

Thus

$$p_{NO_2} = 2x = 2(0.364) = 0.728 \text{ bar}$$

$$p_{N_2O_4} = 2.00 - x = 2.00 - 0.364 = 1.64 \text{ bar}$$

$$\left(\text{Check}: \frac{p_{N_2O_4}}{p^2_{NO_2}} = \frac{1.64}{0.728^2} = 3.09 = K\right)$$

B2. (a) [12 marks] Calculate the pH of s solution made by dissolving 50.0 g of butylaminehydrochloride ($C_4H_9NH_3Cl_{(s)}$) in 1.50 L of water. K_b for butylamine is 4.07 × 10^{-4}.

$$\frac{50.0\,\text{g}}{109.6\,\text{g mol}^{-1}} = 0.456\,\text{mol}\,C_4H_9NH_3Cl$$

But $C_4H_9NH_3Cl_{(s)} \rightarrow C_4H_9NH_3^+{}_{(aq)} + Cl^-{}_{(aq)}$, so $[C_4H_9NH_3^+{}_{(aq)}]$ = 0.456 mol / 1.5 L = 0.304 M

$C_4H_9NH_3^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons C_4H_9NH_{2(aq)} + H_3O^+{}_{(aq)}$

$$K_a(C_4H_9NH^+_{3(aq)}) = \frac{K_w}{K_b(C_4H_9NH_{2(aq)})} = \frac{1.00\times10^{-14}}{4.07\times10^{-4}} = 2.46\times10^{-11}$$

	$[C_4H_9NH_3^+{}_{(aq)}]$	$[C_4H_9NH_{2(aq)}]$	$[H_3O^+{}_{(aq)}]$
Initial	0.304	0	0
Change	–x	+x	+x
Equilibrium	0.304–x	x	x

$$\frac{x(x)}{0.304 - x} = 2.46\times10^{-11} \approx \frac{x^2}{0.304}$$

$$x^2 = 0.304(2.46\times10^{-11})$$

$$x = 2.73\times10^{-6}$$

$$\text{pH} = -\log_{10}(2.73\times10^{-6}) = 5.56$$

(b) [8 marks] Calculate the solubility (in g L^{-1}) of $Ba_3(PO_4)_{2(s)}$ in water. For this compound, K_{sp} = 3.4 × 10^{-23}.

$Ba_3(PO_4)_{2(s)} \rightleftharpoons 3\,Ba^{2+}{}_{(aq)} + 2\,PO_4^{3-}{}_{(aq)}$

If x moles of $Ba_3(PO_4)_{2(s)}$ dissolves, then $[Ba^{2+}{}_{(aq)}]$ = 3x and $[PO_4^{3-}{}_{(aq)}]$ = 2x.
Thus, $K_{sp} = (3x)^3(2x)^2 = 108x^5 = 3.4 \times 10^{-23}$

$$x = \left(\frac{3.4\times10^{-23}}{108}\right)^{1/5} = 1.26\times10^{-5}$$

$$1.26\times10^{-5}\,\text{mol L}^{-1}(601.8\,\text{g mol}^{-1}) = 7.58\times10^{-3}\,\text{g L}^{-1}$$

B3. [20 marks] Calculate the concentrations of all species present (in M) and the pH in a 0.500 M solution of ascorbic acid, $H_2C_6H_6O_6$. For this acid, $K_{a1} = 7.90 \times 10^{-5}$ and $K_{a2} = 1.60 \times 10^{-12}$.
Please put your answers in the boxes at the bottom of this page.

$$H_2C_6H_6O_{6(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HC_6H_6O^-_{6(aq)}$$

	$[H_2C_6H_6O_{6(aq)}]$	$[H_3O^+_{(aq)}]$	$[HC_6H_6O^-_{6(aq)}]$
Initial	0.500	0	0
Change	–x	+x	+x
Equilibrium	0.500–x	x	x

$$\frac{[H_3O^+_{(aq)}][HC_6H_6O^-_{6(aq)}]}{[H_2C_6H_6O_{6(aq)}]} = K_{a_1} = 7.90\times10^{-5}$$

$$\frac{x(x)}{0.500 - x} = 7.90\times10^{-5}$$

$$\frac{x(x)}{0.500} \approx 7.90\times10^{-5} \text{ (because } K_{a_1} < 10^{-3})$$

$$x^2 = 0.500(7.90\times10^{-5})$$

$$x = 6.28\times10^{-3}$$

Thus, $[H_2C_6H_6O_{6(aq)}] = 0.500 - x = 0.500 - 0.00628 = 0.494$ M
$[HC_6H_6O^-_{6(aq)}] = x = 0.00628$ M
$[H_3O^+_{(aq)}] = x = 0.00628$ M
pH = $-\log_{10}[H_3O^+_{(aq)}] = -\log_{10}(0.00628) = 2.20$

$$HC_6H_6O^-_{6(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + C_6H_6O^{2-}_{6(aq)}$$

$$\frac{[H_3O^+_{(aq)}][C_6H_6O^{2-}_{6(aq)}]}{[HC_6H_6O^-_{6(aq)}]} = K_{a_2} = 1.60\times10^{-12}$$

$$[C_6H_6O^{2-}_{6(aq)}] = \frac{K_{a_2}[HC_6H_6O^-_{6(aq)}]}{[H_3O^+_{(aq)}]} = \frac{K_{a_2}(x)}{(x)} = K_{a_2} = 1.60\times10^{-12}\text{ M}$$

$$[OH^-_{(aq)}] = \frac{K_w}{[H_3O^+_{(aq)}]} = \frac{1.0\times10^{-14}}{0.00628} = 1.59\times10^{-12}\text{ M}$$

$[H_2C_6H_6O_{6(aq)}]$	$[HC_6H_6O^-_{6(aq)}]$	$[H_3O^+_{(aq)}]$	$[C_6H_6O^{2-}_{6(aq)}]$	$[OH^-_{(aq)}]$	pH
0.494 M [4 marks]	0.00628 M [4 marks]	0.00628 M [4 marks]	1.60×10^{-12} M [3 marks]	1.59×10^{-12} M [3 marks]	2.20 [2 marks]

B4. (a) [10 marks] Calculate the pH of a solution made by dissolving 1.00 mol butylaminehydrochloride ($C_4H_9NH_3Cl_{(s)}$), and 1.50 mol butylamine ($C_4H_9NH_{2(s)}$) in 2.5 L of water. K_b for $C_4H_9NH_2$ is 4.07×10^{-4}.

$C_4H_9NH_{2(aq)} + H_2O_{(l)} \rightleftharpoons C_4H_9NH_3{}^+{}_{(aq)} + OH^-{}_{(aq)}$
$C_4H_9NH_3Cl_{(s)} \rightarrow C_4H_9NH_3{}^+{}_{(aq)} + Cl^-{}_{(aq)}$

$[C_4H_9NH_{2(aq)}] = 1.50 \text{ mol} / 2.50 \text{ L} = 0.600 \text{ M}$
$[C_4H_9NH_3{}^+{}_{(aq)}] = 1.00 \text{ mol} / 2.50 \text{ L} = 0.400 \text{ M}$

$$\begin{aligned}
pK_a &= 14 - pK_b \\
&= 14 - (-\log_{10}(K_a)) \\
&= 14 - (-\log_{10}(4.07 \times 10^{-4})) = 10.61
\end{aligned}$$

$$\begin{aligned}
pH = pK_a - \log_{10}\left(\frac{[\text{acid}]}{[\text{base}]}\right) \\
= pK_a - \log_{10}\left(\frac{[C_4H_9NH_3{}^+{}_{(aq)}]}{[C_4H_9NH_{2(aq)}]}\right) \\
= 10.61 - \log_{10}\left(\frac{0.400 \text{ M}}{0.600 \text{ M}}\right) \\
= 10.61 - (-0.18) \\
= 10.79
\end{aligned}$$

(b) [10 marks] 0.050 mol $HCl_{(s)}$ is dissolved in 1.00 L of the above buffer solution. Calculate the new pH.
$H_3O^+{}_{(aq)} + C_4H_9NH_{2(aq)} \rightarrow C_4H_9NH_3{}^+{}_{(aq)} + H_2O_{(aq)}$

Thus in 1.00 L of solution, $[C_4H_9NH_3{}^+{}_{(aq)}]$ increases by 0.050 mol/L, and $[C_4H_9NH_{2(aq)}]$ decreases by 0.050 mol/L

The new concentrations are therefore $[C_4H_9NH_3{}^+{}_{(aq)}] = 0.400 + 0.050 = 0.450$ M and $[C_4H_9NH_{2(aq)}] = 0.600 - 0.050 = 0.550$ M

$$\begin{aligned}
&= pK_a - \log_{10}\left(\frac{[C_4H_9NH_3{}^+{}_{(aq)}]}{[C_4H_9NH_{2(aq)}]}\right) \\
&= 10.61 - \log_{10}\left(\frac{0.450 \text{ M}}{0.550 \text{ M}}\right) \\
&= 10.61 - (-0.09) \\
&= 10.70
\end{aligned}$$