Chem 1515
Problem Set #12
Fall 2001

Name_______________________

TA Name ____________________

Lab Section #______

ALL work must be shown to receive full credit. **Due 5:00 pm on Tuesday, November 6, 2001.**

PS12.1. Calculate the pH of a 0.200 M H_3PO_4. Calculate the $[PO_4^{3-}]$ in the solution.

$$H_3PO_{4}(aq) \rightleftarrows H^+(aq) + H_2PO_4^-(aq)$$

initial	.200	1×10^{-7}	0
change	-x	+x	+x x = $[H_3PO_4]_{diss}$
equilibrium	.200 - x	1×10^{-7}+x	0+x

$$K_a = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]}$$

$$7.53 \times 10^{-3} = \frac{x^2}{.200 - x}$$

$$7.53 \times 10^{-3} (0.200 - x) = x^2$$

$$x^2 + 7.53 \times 10^{-3}x - 1.51 \times 10^{-3} = 0$$

solving the quadratic equation $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$x = \frac{-7.53 \times 10^{-3} \pm \sqrt{(7.53 \times 10^{-3})^2 - 4(1)(-1.51 \times 10^{-3})}}{2(1)}$$

$$x = \frac{-7.53 \times 10^{-3} \pm 7.79 \times 10^{-2}}{2}$$

Use only the positive root

$$x = 3.52 \times 10^{-2}\ M = [H^+] = [H_2PO_4^-]$$

$$H_2PO_4^-(aq) \rightleftarrows H^+(aq) + HPO_4^{2-}(aq)$$

initial	3.52×10^{-2}	3.52×10^{-2}	0
change	-x	+x	+x x = $[H_2PO_4^-]_{diss}$
equilibrium	3.52×10^{-2} - x	3.52×10^{-2}+x	0+x

$$K_a = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$6.2 \times 10^{-8} = \frac{3.52 \times 10^{-2}+x \cdot x}{3.52 \times 10^{-2} - x}$$

assume $x << 3.52 \times 10^{-2}$

$$6.2 \times 10^{-8} = \frac{3.52 \times 10^{-2}\,x}{3.52 \times 10^{-2}}$$

6.2×10^{-8} **M** $= x = [HPO_4^{2-}]$,

the $[H^+] = 3.52 \times 10^{-2}\ M + 6.2 \times 10^{-8}\ M = 3.52 \times 10^{-2}\ M$

	$HPO_4^{-}(aq)$	$\rightleftarrows$ $H^+(aq)$	+ $PO_4^{3-}(aq)$	
initial	6.2×10^{-8}	3.52×10^{-2}	0	
change	$-x$	$+x$	$+x$	$x = [HPO_4^{2-}]_{diss}$
equilibrium	$6.2 \times 10^{-8} - x$	$3.52 \times 10^{-2} + x$	$0 + x$	

$$K_a = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]}$$

$$4.2 \times 10^{-13} = \frac{3.52 \times 10^{-2} + x \cdot x}{6.2 \times 10^{-8} - x}$$

assume $x << 3.52 \times 10^{-2}$

$$4.2 \times 10^{-13} = \frac{3.52 \times 10^{-2} x}{6.2 \times 10^{-8}}$$

$$7.4 \times 10^{-19}\ M = x$$

The $[H^+]$ is still 3.52×10^{-2} M so the pH = 1.45. The $[PO_4^{3-}] = 7.4 \times 10^{-19}$ M.

PS12.2. Predict the products of the following neutralization reactions.

a) $HCl(aq) + NaOH(aq) \rightarrow$ **$NaCl(aq) + H_2O(aq)$**

b) **2**$HNO_3(aq) + Ba(OH)_2(aq) \rightarrow$ **$Ba(NO_3)_2(aq) + 2H_2O(aq)$**

c) **2**$NaOH(aq) + H_2CO_3(aq) \rightarrow$ **$Na_2CO_3(aq) + 2H_2O(aq)$**

d) **2**$NH_3(aq) + H_2SO_4(aq) \rightarrow$ **$(NH_4)_2SO_4(aq)$**

e) $HC_6H_5O(aq) + NaOH(aq) \rightarrow$ **$NaC_6H_5O(aq) + H_2O(aq)$**

f) $HCN(aq) + KOH(aq) \rightarrow$ **$KCN(aq) + H_2O(aq)$**

PS12.3. Given a solution containing the following ions (neglect the counter–ion for the moment), write a reaction (with water) and indicate whether the ion acts as an acid or as a base.

a) $F^-(aq)$ + **$H_2O(l) \rightleftarrows HF(aq) + OH^-(aq)$**

b) $ClO_2^-(aq)$**$+ H_2O(l) \rightleftarrows HClO_2(aq) + OH^-(aq)$**

c) $NO_2^-(aq)$ **$+ H_2O(l) \rightleftarrows HNO_2(aq) + OH^-(aq)$**

d) $NH_4^+(aq)$ **$\rightleftarrows NH_3(aq) + H^+(aq)$**

e) $CH_3NH_3^+(aq)$ **$\rightleftarrows CH_3NH_2(aq) + H^+(aq)$**

f) $C_2H_5NH_3^+(aq)$ **$\rightleftarrows C_2H_5NH_2(aq) + H^+(aq)$**

PS12.4. Can you make any generalizations about the acid-base character of the ions in Problem #12.3? If so, state them.

Generally anions act as bases reacting with water to form $[OH^-]$. Cations act as acids reacting with water to form $[H^+]$.

PS12.5. Indicate an acid and a base which could react, in a neutralization reaction, to form each of the following salts. In some cases water will be present as another product.

a) $\mathbf{NaOH}(aq) + \mathbf{HC_6H_7O_6}(aq) \rightarrow NaC_6H_7O_6\,(aq) + \mathbf{H_2O}(l)$

b) $\mathbf{KOH}(aq) + \mathbf{HClO}(aq) \rightarrow KClO(aq) + \mathbf{H_2O}(l)$

c) $\mathbf{(CH_3)_2NH}(aq) + \mathbf{HNO_3}(aq) \rightarrow (CH_3)_2NH_2NO_3(aq)$

d) $\mathbf{NH_3}(aq) + \mathbf{HBr}(aq) \rightarrow NH_4Br(aq)$

e) $\mathbf{KOH}(aq) + \mathbf{HCl}(aq) \rightarrow KCl(aq) + \mathbf{H_2O}(l)$

f) $\mathbf{2NH_3}(aq) + \mathbf{H_2SO_4}(aq) \rightarrow (NH_4)_2SO_4(aq)$

PS12.6. If each salt in Problem 12.5 is added to water, indicate whether the resulting solution is acidic, basic or neutral.

a) $NaC_6H_7O_6(aq) \rightarrow Na^+(aq) + C_6H_7O_6{}^-(aq)$

$C_6H_7O_6{}^-(aq) + H_2O(l) \rightleftarrows HC_6H_7O_6(aq) + OH^-(aq)$ **basic**

b) $KClO(aq) \rightarrow K^+(aq) + ClO^-(aq)$

$ClO^-(aq) + H_2O(l) \rightleftarrows HClO(aq) + OH^-(aq)$ **basic**

c) $(CH_3)_2NH_2NO_3(aq) \rightarrow (CH_3)_2NH_2{}^+(aq) + NO_3{}^-(aq)$

$(CH_3)_2NH_2{}^+(aq) \rightleftarrows (CH_3)_2NH_2(aq) + H^+(aq)$ **acidic**

d) $NH_4Br(aq) \rightarrow NH_4{}^+(aq) + Br^-(aq)$

$NH_4{}^+(aq) \rightleftarrows NH_3(aq) + H^+(aq)$ **acidic**

e) $KCl(aq) \rightarrow K^+(aq) + Cl^-(aq)$ **neutral**

f) $(NH_4)_2SO_4(aq) \rightarrow 2NH_4{}^+(aq) + SO_4{}^{2-}(aq)$

$NH_4{}^+(aq) \rightleftarrows NH_3(aq) + H^+(aq)$ **acidic**

PS12.7. Calculate the pH of the following salt solutions

a) 0.243 M $NaC_6H_7O_6$

	H_2O	+ $C_6H_7O_6{}^-$ ⇄	OH^-	+ $HC_6H_7O_6$	
initial	−−	0.243	0	0	
change	−−	−x	+x	+x	$x = [ClO^-]_R$
final	−−	0.243−x	+x	+x	

$$K_b = \frac{1 \times 10^{-14}}{8 \times 10^{-5}} = \frac{[HC_6H_7O_6][OH^-]}{[C_6H_7O_6{}^-]}$$

$$1.25 \times 10^{-10} = \frac{[x][x]}{[0.243 - x]} \qquad x <<< 0.243$$

$$5.5 \times 10^{-6} = x = [OH^-]$$

$$pOH = 5.26 \qquad pH = 8.74$$

b) 0.319 M $C_5H_5NHClO_4$

	$C_5H_5NH^+$ $\rightleftarrows$	H^+ +	C_5H_5N	
initial	**0.319**	**0**	**0**	
change	**–x**	**+x**	**+x**	$x = [NH_4^+]_D$
equilibrium	**0.319–x**	**+x**	**+x**	

$$K_a = \frac{1 \times 10^{-14}}{1.7 \times 10^{-9}} = \frac{[C_5H_5N][H^+]}{[C_5H_5NH^+]}$$

$$5.88 \times 10^{-6} = \frac{[x][x]}{[0.319-x]} \qquad x<<<0.319$$

$$1.37 \times 10^{-3}\ M = x = [H^+]$$

$$pH = 2.86$$

c) 0.0345 M KCl

pH = 7.00

d) 0.572 M $KC_3H_5O_2$

	H_2O +	$C_2H_3O_2^-$ $\rightleftarrows$	OH^- +	$HC_2H_3O_2$	
initial	**––**	**0.572**	**0**	**0**	
change	**––**	**–x**	**+x**	**+x**	$x = [C_2H_3O_2^-]_R$
final	**––**	**0.572–x**	**+x**	**+x**	

$$K_b = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

$$5.56 \times 10^{-10} = \frac{[x][x]}{[0.572-x]} \qquad x<<<0.572$$

$$1.78 \times 10^{-5} = x = [OH^-]$$

$$pH = 9.25$$

e) 1.00 M $NaHSO_4$

	$HSO_4^- \rightleftarrows$	H^+	+ SO_4^{2-}	
initial	**1.00**	**0**	**0**	
change	**–x**	**+x**	**+x**	$x = [HSO_4^-]_R$
final	**1.00 – x**	**+x**	**+x**	

$$K_a = 1.2 \times 10^{-2} = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

$$1.2 \times 10^{-2} = \frac{[x][x]}{[1.00 - x]}$$

$$1.2 \times 10^{-2}(1.00 - x) = x^2$$

$$x^2 + 1.2 \times 10^{-2}x - 1.2 \times 10^{-2} = 0$$

solving the quadratic equation $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$x = \frac{-1.2 \times 10^{-2} \pm \sqrt{(1.2 \times 10^{-2})^2 - 4(1)(-1.2 \times 10^{-2})}}{2(1)}$$

$$x = \frac{-1.2 \times 10^{-2} \pm 0.219}{2}$$

Use only the positive root

$$x = 0.104 \text{ M} = [H^+]$$
$$pH = 0.983$$

PS12.8. In the series of oxyacids, XOH, OXOH, and O_2XOH, list the acids in order of increasing acid strength. Justify your answer.

XOH < OXOH < $\mathbf{O_2XOH}$

As the number of oxygen atoms bonded to the central atom, X, increases, the more electron density is removed from the O–H bond. The smaller electron density decreases the strength of the O–H bond resulting in a larger ionization of the proton, increasing the acidity of the substance.